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MAY 80 C J SCHACK, K O CHRISTE F49620-77-C-0036

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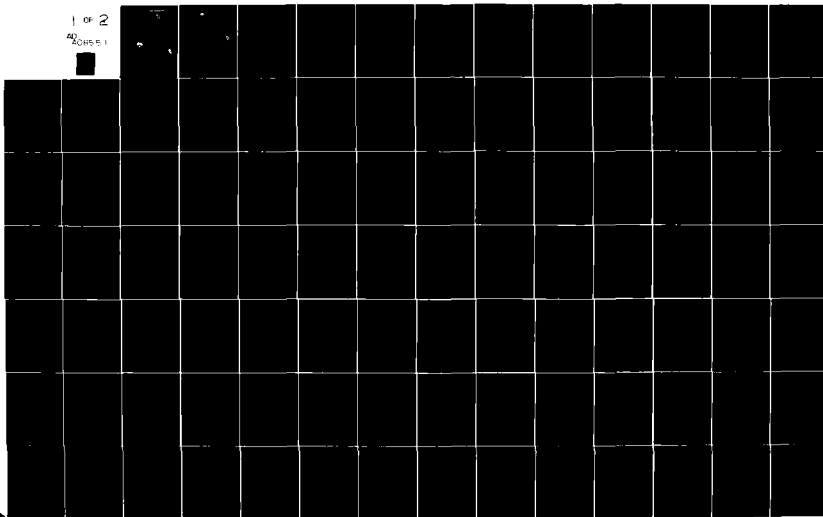
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INORGANIC REACTANTS FOR SYNTHESIS
OF NOVEL FLUOROCARBON DERIVATIVES

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Several different fluorocarbon fluids containing the SF₅O- and CF₃O- groups have been prepared using fluoroolefins and either SF₅OOSO₂F or CF₃OOSO₂F. In addition the fluorocarbon ethers, SF₅OC₂F₄OSO₂F and CF₃OC₂F₄OSO₂F, and several of their derivatives were prepared and characterized. Chlorine fluorosulfate and bromine fluorosulfate were shown to have wide utility in the displacement of halide from fluorocarbon halides (R₃X) resulting in the formation of fluorocarbon fluorosulfates. The R₃SO₃F compounds are readily converted to derivatives such as acid fluorides, acids, etc., and in this way functionality		

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is introduced into relatively inert fluorocarbons. Furthermore both Cl- and BrSO_3F readily react with fluorocarbon acids and derivatives resulting in the loss of CO_2 and the formation of RfX ($\text{X}=\text{Cl}, \text{Br}$) species. Together, the conversion of RfCF_2X to $\text{RfCF}_2\text{SO}_3\text{F}$, followed by hydrolysis of $\text{RfCF}_2\text{SO}_3\text{F}$ to RfCO_2M and decarboxylation with XSO_3F to give RfX , represents a new high yield chain shortening process. New procedures for synthesizing iodine fluorosulfate were developed. Previously unknown olefin addition reactions of ISO_3F were discovered which furnish potentially useful difunctional derivatives. Chlorine nitrate oxidation of iodine in $i\text{-C}_3\text{F}_7\text{I}$ gave a new, thermally stable bis-nitrate compound. The necessity for iso-RfI in forming these stable bis-adducts was demonstrated. A new method was discovered for the introduction of fluorine into an aromatic ring with retention of aromaticity, using NF_4BF_4 in HF solution. Also when the arene is already highly fluorinated, it was shown that a slower addition of fluorine occurred to give cyclohexadienes and cyclohexenes.

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FOREWORD

The research reported herein was supported by the U. S. Air Force Office of Scientific Research under Contract No. F49620-77-C-0038, with Dr. A. J. Matuszko as Scientific Officer. This report covers the period 15 March 1978 through 14 March 1980. Dr. C. J. Schack was the Program Engineer. The scientific effort was carried out by Dr. C. J. Schack and K. O. Christe. The program was administered by Dr. L. R. Grant, Program Manager, Chemistry Programs Advanced Programs.

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INTRODUCTION

This report covers a 3-year period and describes Rocketdyne's research efforts in the area of inorganic reagents applied to the synthesis of novel fluorocarbons which have potential military and space applications. The objectives of this program were:

1. Study the synthesis and properties of fluorocarbon model compounds containing $\text{CF}_3\text{O}-$ and $\text{SF}_5\text{O}-$ substituents and the development of preparative routes for $\text{SF}_5\text{O}-$ substituted perfluoroalkyl ethers.
2. Conduct an investigation into the possible synthesis of $\text{SF}_5\text{O}-$ substituted fluorocarbon fluorosulfates as monomers, prepolymers, and/or crosslinkers.
3. Investigate the reaction chemistry of inorganic reagents for development of novel synthetic methods for selective introduction of fluorine into fluorocarbons including aromatics.

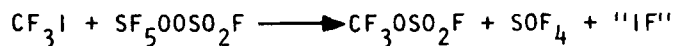
Most of the objectives have been accomplished and much useful information has been obtained toward a better understanding of the relevant chemistry. These results are described in detail in this report.

DISCUSSION

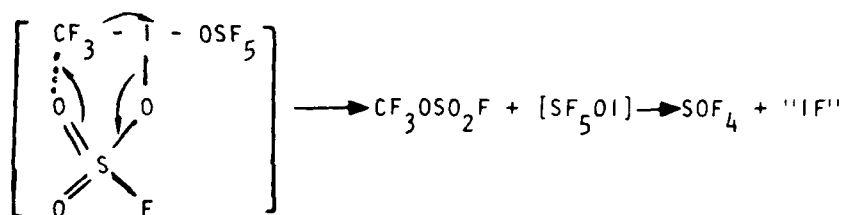
SF₅O- AND CF₃O- CHEMISTRY

An area of prime interest to this program was that aimed at the incorporation of SF₅O- ligands into fluorocarbon backbones to improve their useful properties while retaining their demonstrated chemical inertness. Several inorganic SF₅O- species are known which have potential in this regard. These include SF₅OCl, SF₅OOSO₂F, SF₅OOSF₅, and SF₅OF. Based on our successful work with related "positive" chlorine species such as ClOCIO₃ and ClOSO₂F (Refs. 1, 2, and References therein), reaction of SF₅OCl and fluorocarbon halides was anticipated as a possible route to R_fOSF₅ derivatives. However, the substrates CF₃CFBrCF₂Br, CF₃I, and i-C₃F₇I, investigated in this regard failed to undergo the desired substitution. The bromine material catalyzed the decomposition of SF₅OCl, while the iodides underwent fluorination to R_fIF₂ species. In view of the fact that Br and I should be about the most easily displaced ligands in fluorocarbons, additional substrates such as chlorides were not tested. It appears therefore that SF₅OCl is not useful in such displacements under the present conditions.

Improved syntheses of SF₅OOSO₂F, SF₅OOSF₅, and FO₂SOSO₂F were developed under this contract and have been described in manuscripts form (Appendix A). The mixed peroxide, SF₅OOSO₂F, was reacted with CF₃I as a possible means of substituting iodine by SF₅O-. At ambient temperature the observed reaction was:



Since iodine is readily oxidized to the +III oxidation state, the following mechanism appears plausible. It involves the oxidative addition of -OSF₅ and -OSO₂F to the iodine atom, followed by an intramolecular rearrangement, SF₅OI elimination, and decomposition of the latter.



Attempts to alter or prohibit this mode of reaction by lowering the temperature failed, and the system was abandoned for its lack of potential with respect to generation of R_fOSF_5 compounds.

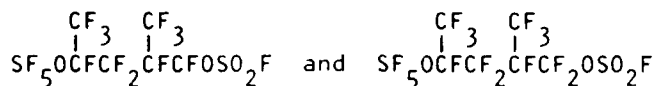
A third $\text{SF}_5\text{O}-$ compound examined as a source of this group into fluorocarbons via substitution reactions was SF_5OOSF_5 . However, the thermal activation required (155°C), to achieve reaction was too great to allow simple substitution to occur. Instead uncontrolled fluorination was observed producing CF_4 as the only carbon containing derivative.

In summary, it has been demonstrated that the synthesis of $\text{SF}_5\text{O}-$ fluorocarbons via substitution reactions employing thermal activation is not a viable scheme. This applies to all three of the tested $\text{SF}_5\text{O}-$ sources, SF_5OCl , $\text{SF}_5\text{OOSO}_2\text{F}$, and SF_5OOSF_5 .

ADDITION REACTIONS

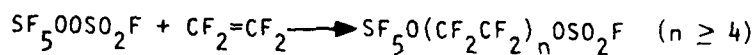
While substitution reactions were not effective, several addition reactions yielded products which incorporate the $\text{SF}_5\text{O}-$ group into fluorocarbons. The efficiency of $\text{SF}_5\text{OOSO}_2\text{F}$ in adding to olefins was discovered on this program (Ref. 3). To date, this reaction has been carried out successfully utilizing three olefins, $\text{CF}_3\text{CF}=\text{CF}_2$, $\text{CF}_2=\text{CF}_2$, and $\text{CF}_2=\text{CFCl}$, as substrates. Several reactions of the first two were studied under varying conditions to determine possible product variance. With hexafluoropropylene at room temperature, no reaction with the mixed peroxide was observed. However, a reaction occurred readily at 95°C . The tendency was for more of the olefin to be consumed on a molar basis than the

peroxide, indicating the formation of telomer products. While on one occasion it appeared that a nearly 1:1 addition occurred, it was not possible to duplicate that result. Rather the adducts were of the type $\text{SF}_5\text{O}-(\text{C}_3\text{F}_6)_n-\text{OSO}_2\text{F}$ wherein $n=2-4$. At a reaction temperature of 35 to 40 C the degree of telomerization was lowered to about 2. Partial separation of the more volatile components and examination by infrared, mass, and ^{19}F nmr spectroscopy have shown two isomers to be the main products.



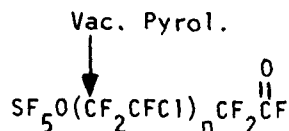
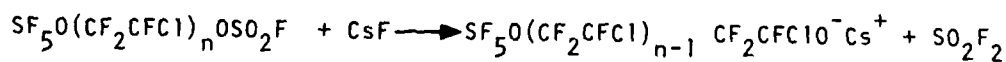
Because the nmr spectra are second order, their analysis is exceedingly complex, a situation exacerbated by the presence of isomer mixtures. Preparations using a large excess of $\text{SF}_5\text{OSO}_2\text{F}$ relative to C_3F_6 were also tried, with the aim of minimizing oligomer formation by limiting the amount of available olefin (Ref. 4). Separation of the addition products was attempted by gas chromatography using two different column packings, Chromosorb-T and Poropak PS, at several temperatures. Unfortunately, a clean separation of components was not realized. Three relatively minor forepeaks were generally followed immediately by two major peaks of similar area but these were not adequately separated to afford pure material for definitive characterization. In addition, under some GC conditions, the second major peak showed a tail indicating still another component was present. Although these SF_5O^- containing oligomers could not be successfully separated under the conditions described above, their excellent thermal stability (no decomposition being noted in several days at 150 to 200 C even in the presence of strong oxidizing agents such as BrSO_3F and $\text{S}_2\text{O}_6\text{F}_2$) indicates the usefulness of these compounds.

With tetrafluoroethylene, $\text{SF}_5\text{OOSO}_2\text{F}$ addition was observed at 115 C, ambient temperature, or even -10 C. Originally a colorless, liquid product was obtained, but with a high degree of telomerization.



Vacuum distillation of lower molecular weight fractions was attempted and was partially successful. However, too little material was obtained for a practical study. In an effort to secure more material additional syntheses were conducted at room temperature. For reasons as yet unclear, these preparations gave more extensive polymerization than before, $n \geq 15$ based on material balance. These reactions gave, essentially no liquid adducts, but rather a white solid which appears spectroscopically as an $\text{SF}_5\text{O}-$ and $-\text{OSO}_2\text{F}$ end capped Teflon. Variations in reactant ratio and even lower temperature were then employed to preclude polymerization. Some liquid product was obtained; however, GC separations presented the same problem encountered with the propylene derivatives. An alternate path to the parent compound ($n=1$) was developed (see below).

The reaction of chlorotrifluoroethylene with $\text{SF}_5\text{OOSO}_2\text{F}$ has only been examined at 115 C. As with the other olefins, addition occurred but oligomers formed. These were again, colorless, viscous fluids of low volatility whose infrared spectra showed all the expected features of $\text{SF}_5\text{O}(\text{CF}_2\text{CFCl})_n\text{OSO}_2\text{F}$ type materials. These products were also shown to undergo the expected (Ref. 1) CsF catalyzed elimination of SO_2F_2 .



No evidence of any other degradation was obtained, indicating that the $\text{SF}_5\text{O}-$ group was unaffected by this procedure. Acyl fluorides are, of course, useful starting materials for several other functionalities or anionic polymerizations (Ref. 5).

DENSITIES OF $\text{SF}_5\text{O}-$ SUBSTANTIAL FLUOROCARBONS

One of the useful properties of fluorocarbon materials is their high density and one of the principal reasons for wanting to incorporate $\text{SF}_5\text{O}-$ groups into fluorocarbons is to obtain still higher density materials. In order to determine initially the approximate impact of an $\text{SF}_5\text{O}-$ group on the density of a simple fluorocarbon, the density of one of the compounds ($\text{SF}_5\text{O}-\text{C}_2\text{F}_4\text{Cl}$) prepared on this program was measured ($d_{40} = 1.820 - 0.0027 t_c$). Comparison to similar compounds which have been reported (Refs. 6 to 8) are given in Table 1.

TABLE 1. LIQUID DENSITIES (20 C)*

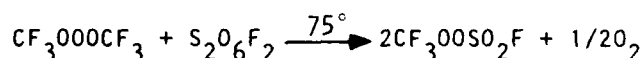
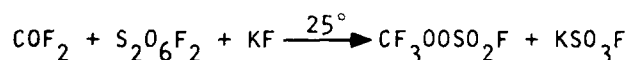
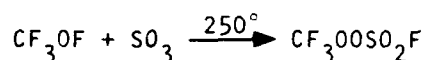
CF_3Br	1.58	CF_3OSF_5	~1.57
$\text{C}_2\text{F}_5\text{Br}$	1.65	$\text{C}_2\text{F}_5\text{OSF}_5$	~1.61
$\text{ClC}_2\text{F}_4\text{Br}$	1.8 (est.)	$\text{ClC}_2\text{F}_4\text{OSF}_5$	1.77
FO_3SBr	2.25	FO_3SOSF_5	1.84
Br-Br	3.12	$\text{F}_5\text{S00SF}_5$	1.96

*All values were corrected for 20 C

From the data it is apparent that incorporation of the $\text{SF}_5\text{O}-$ group into simple fluorocarbons increases the density by about the same amount as a bromine substituent.

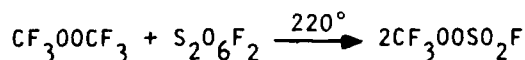
CF₃O- Substituted Fluorocarbons

One of the objectives of this program was the synthesis of CF₃O- analogues of the SF₅O- containing species. This should allow comparison of properties of compounds containing one of these two substituents. Accordingly, the preparation of CF₃OOSO₂F was undertaken for use as a reactant with olefin substrates. Three literature reports concerning the synthesis of this compound are illustrated by the equations.



The first equation, while elegantly simple, suffers from a poor yield (Ref. 9). In the second equation, a better yield is reported (50%) (Ref. 10) but as we have observed (Ref. 2) in the case of SF₅OOSO₂F, this three-component system requires precise conditions for good results. A better yield (87%) was obtained with the third reaction (Ref. 11). Unfortunately, the trioxide reactant is not readily available.

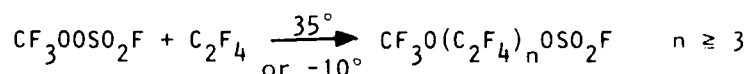
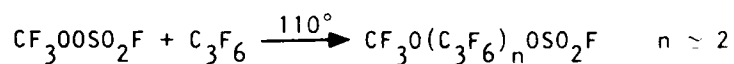
Another possible reaction was considered which was based on the use of SO₃F radicals generated from S₂O₆F₂ as scavengers for CF₃O radicals generated from CF₃OOCF₃ (Ref. 12).



Reputedly this process is quantitative and it was used by those authors as a trap and measure of the production of CF₃O in a kinetic study of the pyrolysis of CF₃OOCF₃. Obviously, it should also be of synthetic utility, and it was examined in that regard by us. It was found that using

stainless steel cylinders as containers, vs the nickel vessel of Descamps and Forst (Ref. 12), the optimum conversion and yield of $\text{CF}_3\text{OOSO}_2\text{F}$ was attained at 240 to 250 C in about 16 hours. The yields were generally 50 to 70% and some recycling of unreacted starting materials was possible. Thus, this reaction served for this preparation. An attempt was made to apply this thermal process for the generation of $\text{SF}_5\text{OOSO}_2\text{F}$ from SF_5OOSF_5 and $\text{S}_2\text{O}_6\text{F}_2$; however, the maximum yield realized was only 47% and it was not pursued any further.

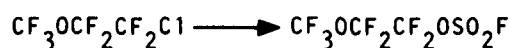
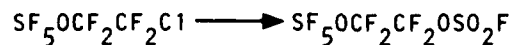
Investigation of olefin reactions of $\text{CF}_3\text{OOSO}_2\text{F}$ have been made with tetrafluoroethylene and hexafluoropropylene.



These results parallel closely those found for similar $\text{SF}_5\text{OOSO}_2\text{F}$ systems. The tendency to telomerize appears about equal under comparable conditions. Generally, these products are again low volatility, thermally stable, colorless liquids. Partial separation by fractional condensation is possible. The compounds of lower n obtained thereby, when examined spectroscopically, appear to contain always one $\text{CF}_3\text{O}-$ and one $-\text{SO}_2\text{F}$ unit in each chain for the $n=1-3$ range investigated.

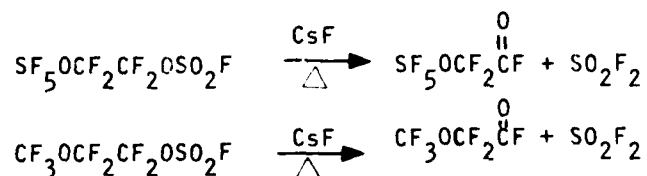
INTRODUCTION OF FUNCTIONAL GROUPS

Finally, in the areas of $\text{SF}_5\text{O}-$ and $\text{CF}_3\text{O}-$ chemistry, the functionalization of simple, known $\text{SF}_5\text{O}-$ and $\text{CF}_3\text{O}-$ fluorocarbons was investigated. Thus $\text{SF}_5\text{OCF}_2\text{CF}_2\text{Cl}$ and $\text{CF}_3\text{OCF}_2\text{CF}_2\text{Cl}$ (Refs. 13, 14) were prepared and reacted with $\text{ClSO}_3\text{F}/\text{Br}_2$ at 140 C to substitute $-\text{Cl}$ with $-\text{OSO}_2\text{F}$.

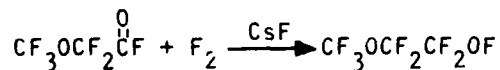


This conversion was successful and infrared spectra of the products are given in Fig. 1 and 2. These spectra are presented as an illustration of the utility of infrared spectroscopy in identifying the important groups in this simple molecule. Thus in the $\text{SF}_5\text{O}-$ compound, the SO_2 stretch in $-\text{OSO}_2\text{F}$ is at 1499 cm^{-1} , the C-F stretches at $1300\text{--}1200\text{ cm}^{-1}$, the C-O stretch at 1088 cm^{-1} , the S-F stretches (for $-\text{OSO}_2\text{F}$ and $\text{SF}_5\text{O}-$) in the range $950\text{--}900\text{ cm}^{-1}$, the S-O stretch at 862 cm^{-1} , and the important SF_4 bending mode at 586 cm^{-1} . The analogous material, $\text{SF}_5\text{O}(\text{CF}_2\text{CF}_2)_n\text{OSO}_2\text{F}$, derived from $\text{SF}_5\text{OOSO}_2\text{F}$ and $\text{CF}_2=\text{CF}_2$ has the same important bands with increased C-F band intensity due to n being greater than one and somewhat broadened bands owing to the liquid/solid physical state of the samples.

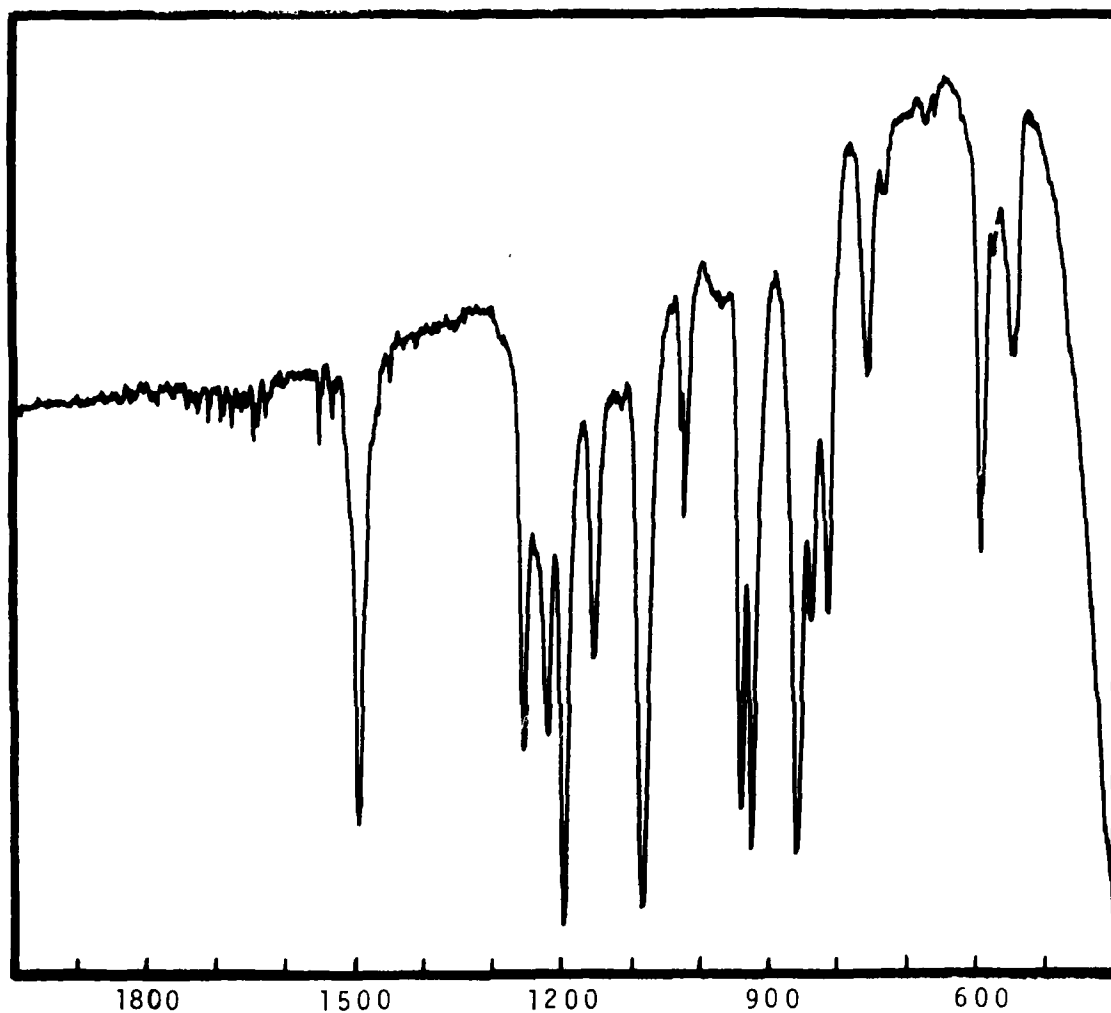
These new fluorocarbon fluorosulfates are readily converted to the corresponding acyl fluorides as shown.



This is a nearly quantitative reaction and its course is easily followed via infrared spectroscopy as shown in Fig. 3 and 4. The disappearance of the $-\text{SO}_3\text{F}$ group bands is evident and the appearance of the C=O stretch of the acyl fluoride at $\sim 1900\text{ cm}^{-1}$ is obvious. Still another derivative is the hypofluorite which was made by the reaction:

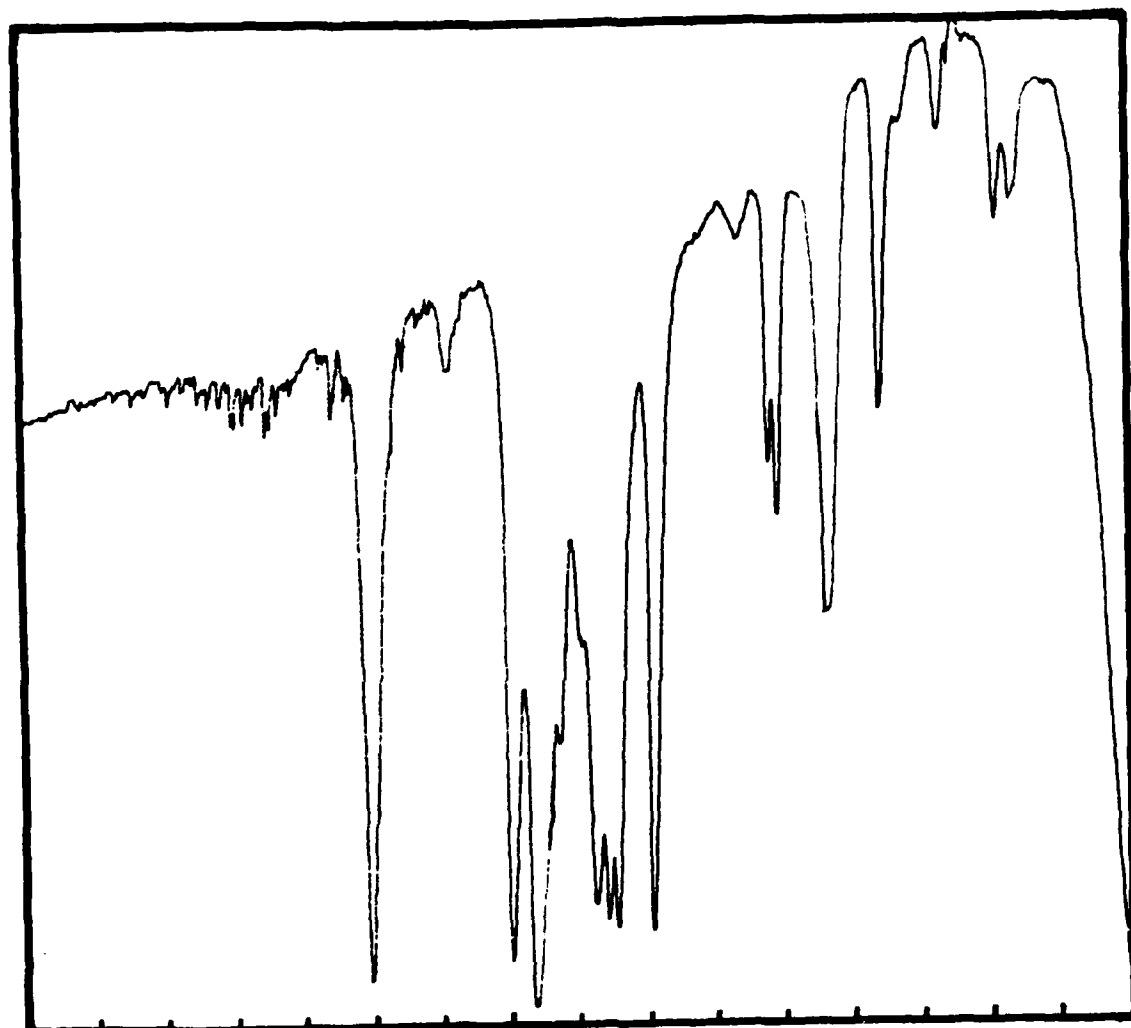


The infrared spectrum of this compound is shown in Fig. 5 wherein the absence of the C=O absorption and the appearance of the weak $-\text{OF}$ stretch at 895 cm^{-1} is noteworthy.



WAVENUMBER (cm^{-1})
 $\text{SF}_5\text{OCF}_2\text{CF}_2\text{SO}_3\text{F}$ (4 mm)

Figure 1. $\text{SF}_5\text{OCF}_2\text{CF}_2\text{SO}_3\text{F}$



1800

1500

1200

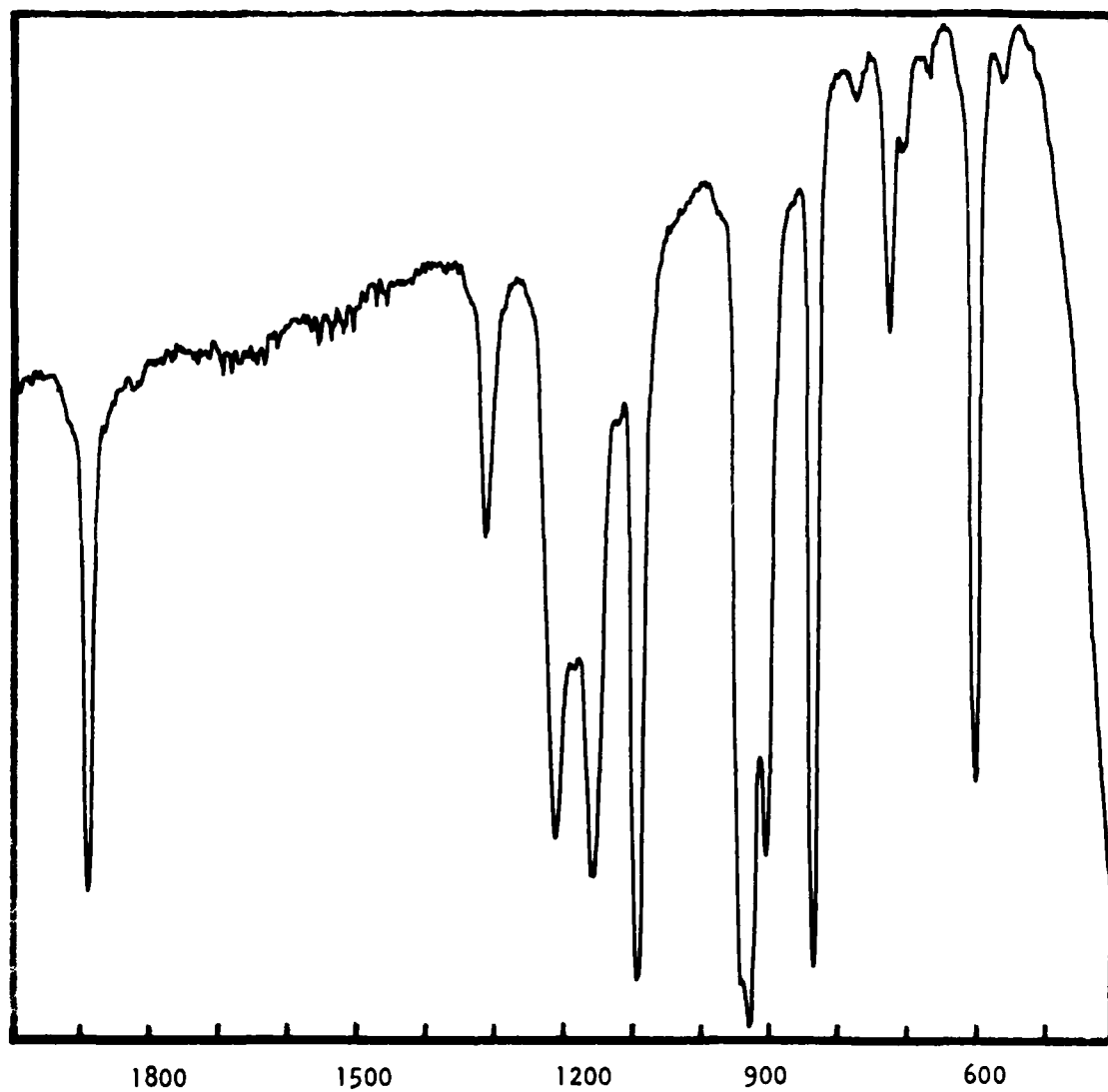
900

600

WAVENUMBER (cm⁻¹)

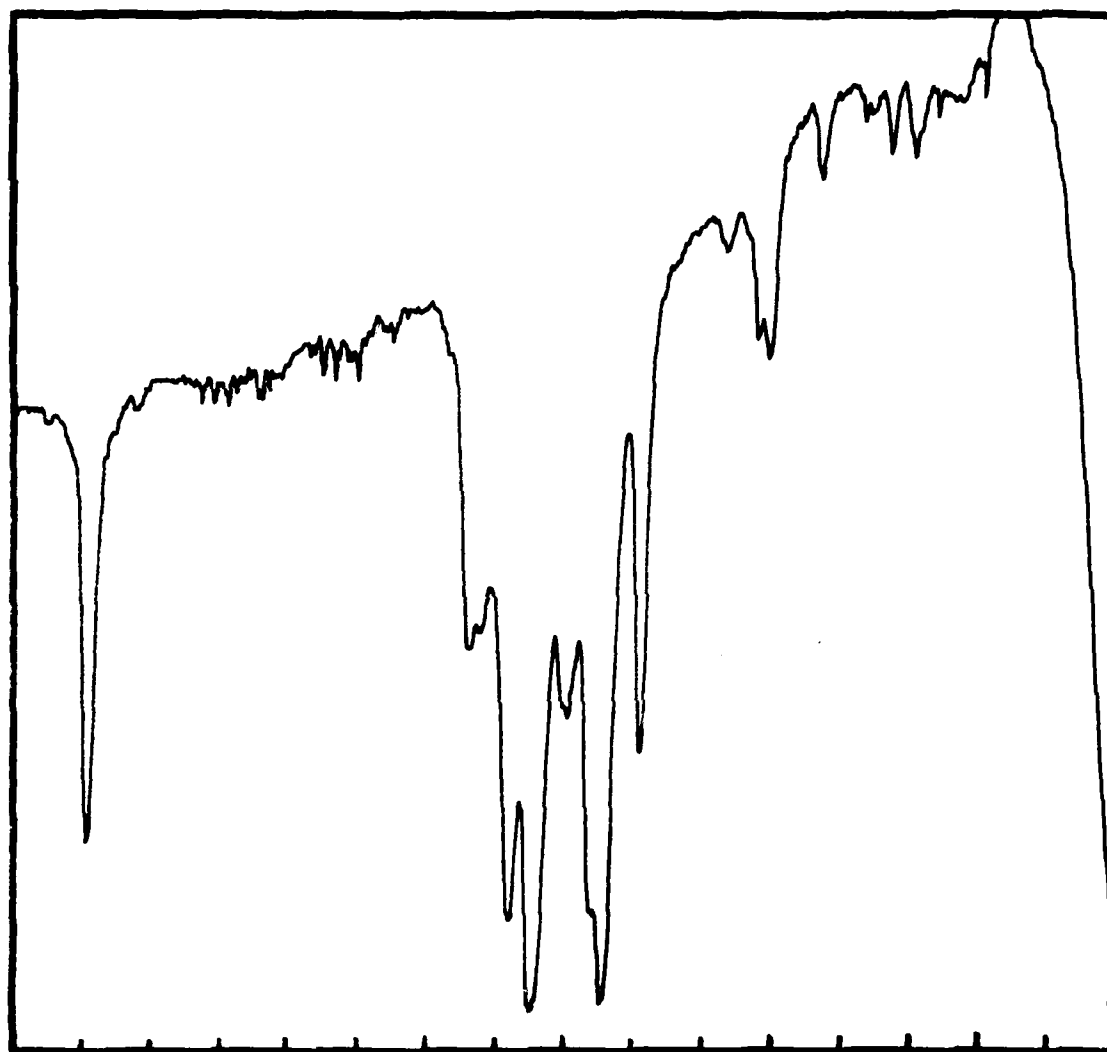
CF₃OCF₂CF₂SO₃F (6 mm)

Figure 2. CF₃OCF₂CF₂SO₃F



WAVENUMBER (cm^{-1})
 $\text{SF}_5\text{OCF}_2\text{CFO}$ (8 mm)

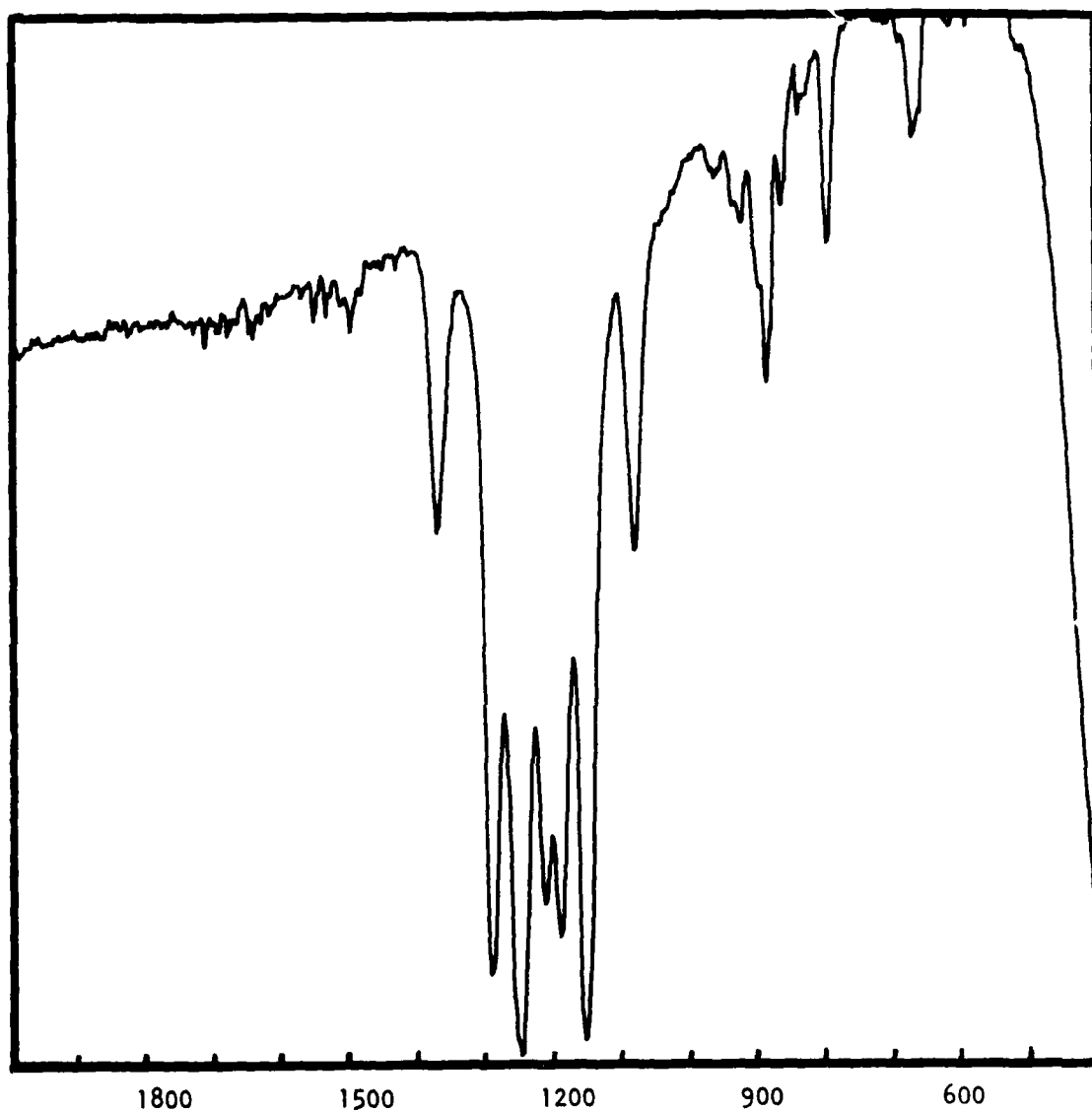
Figure 3. $\text{SF}_5\text{OCF}_2\text{CFO}$



WAVENUMBER (cm^{-1})
 $\text{CF}_3\text{OCF}_2\text{CFO}$ (9 mm)

Figure 4. $\text{CF}_3\text{OCF}_2\text{CFO}$

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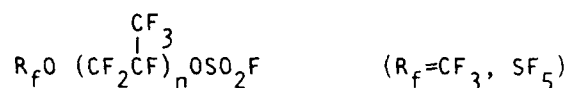


WAVENUMBER (cm^{-1})

$\text{CF}_3\text{OCF}_2\text{CF}_2\text{OF}$ (8 mm)

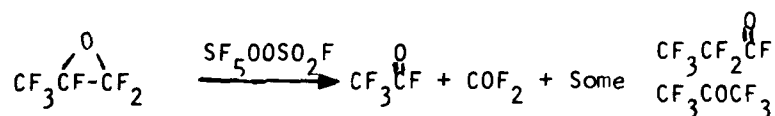
Figure 5. $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OF}$

Tables 2 and 3 give the observed ions in the mass spectra of several of the $\text{SF}_5\text{O}-$ and $\text{CF}_3\text{O}-$ species, both monomers and telomers. It is evident that parent ions are not seen while nearly all other likely ion fragments are formed. When only limited numbers of CF_3 groups are present in a compound which contains an SF_5 group, then the latter is the base peak. From the presence of the $\text{C}_2\text{F}_4\text{SO}_3\text{F}^+$ ion in both $\text{CF}_3\text{O}(\text{C}_3\text{F}_6)_n\text{SO}_3\text{F}$ and $\text{SF}_5\text{O}(\text{C}_3\text{F}_6)_n\text{SO}_3\text{F}$ together with $\text{CF}_3\text{OCF}_2^+$ and $\text{SF}_5\text{OCF}_2^+$ ions it can be deduced that these telomers have mainly the structure illustrated.



Only low intensity peaks assignable to $\text{R}_f\text{OC}_2\text{F}_4^+$ ions were observed. These reactions and additional characterizing data for the new compounds are described more fully in manuscript form in Appendix C. These materials are expected to be useful intermediates for reaction with epoxides and olefins in ether formation (Ref. 1).

In addition to the olefin systems, the interaction of $\text{SF}_5\text{OOSO}_2\text{F}$ and hexafluoropropylene oxide (HFPO) was examined. At room temperature no reaction occurred and at 95°C very little $\text{SF}_5\text{OOSO}_2\text{F}$ reacted, but all the HFPO was destroyed.



Involvement of the peroxide in this cleavage was evidenced by the formation of some COF_2 . Generally HFPO in the absence of oxygen sources thermally degrades to CF_3COF and $:\text{CF}_2$ (observed as $\text{CF}_2=\text{CF}_2$ and $\text{c-C}_3\text{F}_6$) (Ref. 15). The failure of HFPO to form an adduct with the peroxide under these radical conditions is in keeping with its normal behavior (Ref. 5). It is very reactive under many other conditions.

TABLE 2. MASS SPECTRA OF CF3O- AND SF5O- FLUOROCARBONS

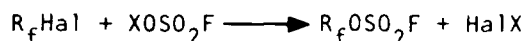
$\text{CF}_3\text{OCF}_2\text{CF}_2\text{SO}_3\text{F}$	$\text{CF}_3\text{O}(\text{C}_3\text{F}_6)_n\text{SO}_3\text{F}$	$\text{SF}_5\text{O}(\text{C}_3\text{F}_6)_n\text{SO}_3\text{F}$
$\text{CF}_3\text{OC}_2\text{F}_4\text{SO}_3^+$ $\text{CF}_3\text{OC}_2\text{F}_4\text{SOF}^+$ $\text{CF}_3\text{OC}_2\text{F}_4\text{SO}_2^+$ $\text{C}_2\text{F}_4\text{SO}_3\text{F}^+$ $\text{CF}_3\text{OC}_2\text{F}_4^+$	$(\text{C}_3\text{F}_6)_n\text{SO}_3\text{F}^+ (n=1,2)$ $\text{CFO}(\text{C}_3\text{F}_6)_n\text{O}^+$ $(\text{C}_a\text{F}_{2a+1})^+ (a=1-6)$ $(\text{C}_a\text{F}_{2a-1})\text{O}^+$ $\text{CF}_3\text{O}(\text{C}_3\text{F}_6)\text{O}^+$ $\text{CF}_3\text{O}(\text{C}_3\text{F}_5)\text{O}^+$	$(\text{C}_3\text{F}_6)_n\text{SO}_3\text{F}^+ (n=1,2)$ $(\text{C}_a\text{F}_{2a+1})^+ (a=1,6)$ $(\text{C}_a\text{F}_{2a-1})\text{O}^+$ $\text{SF}_5\text{O}(\text{C}_3\text{F}_6)^+$
$\text{CF}_3\text{O}(\text{C}_2\text{F}_3)\text{O}^+$ $\text{CF}_3\text{O}(\text{C}_2\text{F}_2)\text{O}^+$ $\text{CF}_2\text{SO}_3\text{F}^+$ $\text{CF}_3\text{OCF}_2^+$ CF_3OCF^+	$(\text{CF}_2)_n\text{SO}_3\text{F}^+$ $\text{CF}_3\text{OCF}_2^+$ CF_3OCF^+	$(\text{CF}_2)_n\text{SO}_3\text{F}$ $\text{SF}_5\text{OCF}_2^+$ $\text{SF}_5^+ \text{Base}$
SO_2F_2^+ C_2F_4^+ $\text{C}_2\text{F}_3\text{O}^+$	SO_2F_2^+ C_2F_4^+ $\text{C}_2\text{F}_3\text{O}^+$ C_3F_3^+	SF_3O^+ SO_2F_2^+ C_2F_4^+ $\text{C}_2\text{F}_3\text{O}^+$ C_3F_3^+ SF_3^+ SF_2O^+
SO_2F^+	SO_2F^+	SO_2F^+
$\text{CF}_3^+ \text{Base}$ SOF^+	$\text{CF}_3^+ \text{Base}$ SOF^+	SF_2^+ CF_3^+ SOF^+

TABLE 3. MASS SPECTRA OF SF50- FLUOROCARBONS

<u>SF₅OCF₂C(O)F</u>	<u>SF₅OC₂F₄OSO₂F</u>	<u>SF₅O(C₂F₄)_nOSO₂F</u> n=1-4
	SF ₅ OC ₂ F ₄ OSO ₂ ⁺ vw	(C ₂ F ₄) _n OSO ₂ F ⁺
	SF ₅ OC ₂ F ₄ SOF ⁺ vw	(C _n F _{2n+1}) ⁺
		(C _n F _{2n-1} O) ⁺
		(C _n F _{2n-1}) ⁺
	C ₂ F ₄ OSF ₅ ⁺	C ₂ F ₄ OSF ₅ ⁺
	C ₂ F ₄ OSO ₂ F ⁺	C ₂ F ₄ OSO ₂ F ⁺
CF ₂ OSF ₅ ⁺	CF ₂ OSF ₅ ⁺	CF ₂ OSF ₅ ⁺
	CF ₂ OSO ₂ F ⁺	CF ₂ OSO ₂ F ⁺
SF ₅ ⁺ BASE	SF ₅ ⁺ BASE	SF ₅ ⁺ BASE
SF ₃ O ⁺	SF ₃ O ⁺	SF ₃ O ⁺
C ₂ F ₃ O ⁺	SF ₃ ⁺	SF ₃ ⁺
SF ₃ ⁺	SO ₂ F ⁺	SO ₂ F ⁺
CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺
SOF ⁺	SOF ⁺	SOF ⁺

FLUOROCARBON HALIDE-HALOGEN FLUOROSULFATE REACTIONS

Mono - or multifunctional fluorocarbons are of utmost importance as monomers, crosslinking agents, etc. in fluorocarbon elastomer chemistry. Previously (Ref. 1) we had shown the utility of a new and simple method for introducing functional groups into fluorocarbon chains and for step-wise shortening of those chains. This work was continued and its scope more carefully defined. The types of reaction were:

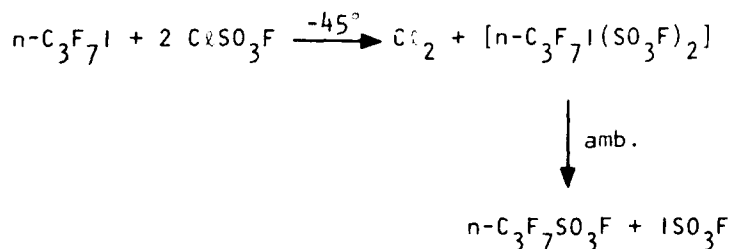


The $R_f\text{Hal}$ moieties are generally unreactive chlorides and bromides. Several examples of this reaction have been elucidated. From these results, it is evident that primary Cl can only be displaced by $-\text{SO}_3\text{F}$ with difficulty or not at all. Furthermore, it can be seen that secondary Br and Cl are not affected under comparable conditions. However, primary Br is easily displaced. Also it was shown that in situ generation of BrSO_3F by adding of small amounts of Br_2 to the reaction mixture enhanced the displacement reaction. Even under these rigorous conditions, no C-C bond cleavage occurred nor were ether functions such as $\text{CF}_3\text{O}-$ or $\text{SF}_5\text{O}-$ in proximity to the displaced Cl disrupted (Appendix C).

Fluorocarbon iodides and ClSO_3F reacted at low temperature to give at least formally the iodine (III) oxidation product of empirical formula, $R_f\text{I}(\text{SO}_3\text{F})_2$. If a primary iodide was used, the iodine (III) derivative decomposed at ambient temperature to provide the $R_f\text{SO}_3\text{F}$ moiety in good yield. If a secondary iodide was used, a thermally stable, salt-like product resulted: $[(i\text{-C}_3\text{F}_7)_2\text{I}]^+[\text{I}(\text{SO}_3\text{FO}_4)]^-$. The scope and utility of this halogen fluorosulfate displacement of halide from fluorocarbon chlorides, bromides, and iodides is fully described in manuscript form in Appendix D.

Although the oxidation of iodine in $i\text{-C}_3\text{F}_7\text{I}$, to stable solid derivatives, has now been demonstrated for several cases (Ref. 3), it remained to be

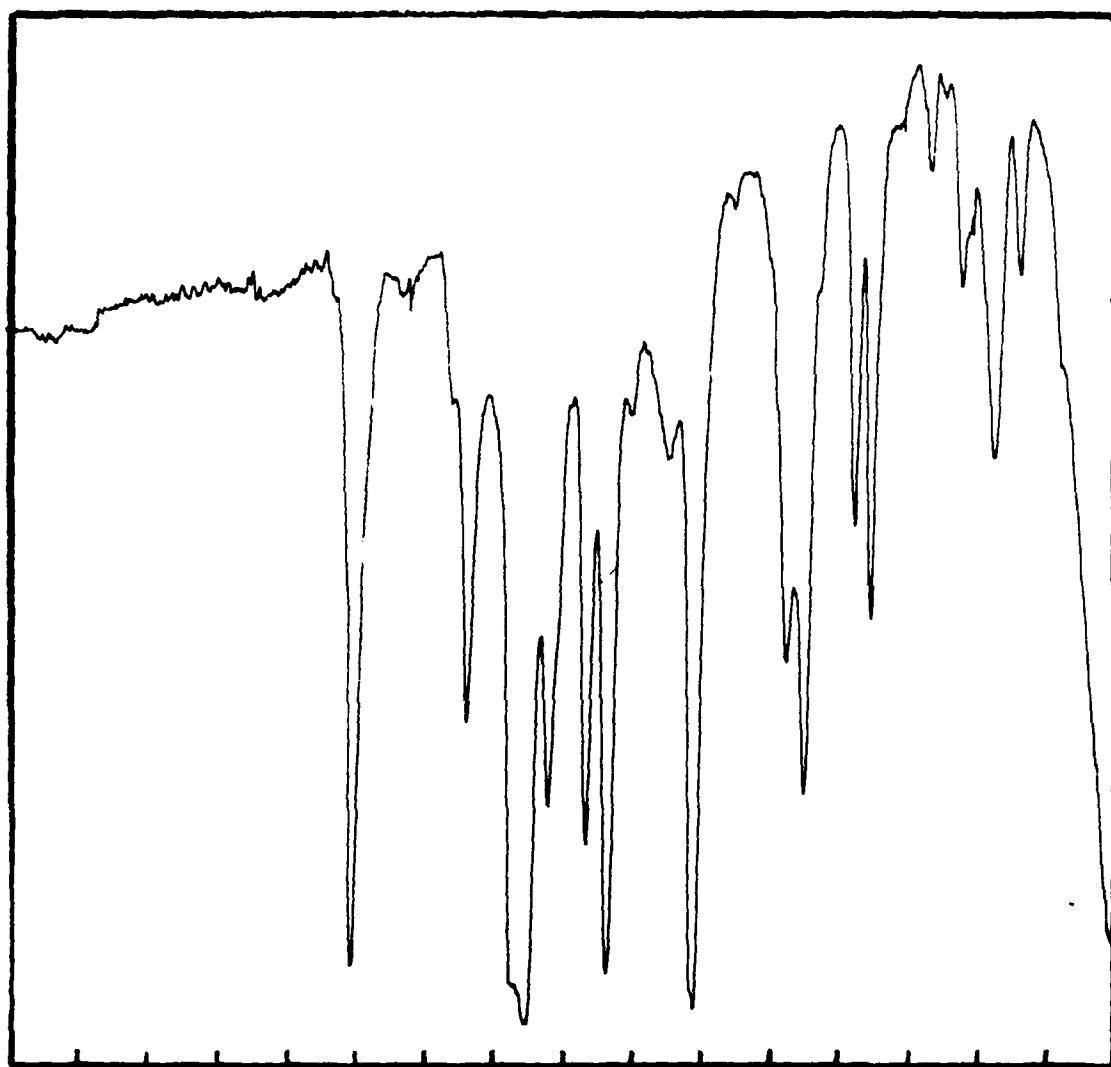
shown that this behavior is the result of iodine being a secondary substituent. Thus several primary R_fI substrates had been shown to give unstable oxidative adducts that decomposed to new substituted R_f species. However, no secondary-iodo isomer of these R_f 's, nor the primary counterpart of $i-C_3F_7I$, had been tested to determine if this unusual behavior is specific to the secondary iodide. Therefore a sample of $n-C_3F_7I$ was reacted in the usual manner with a two-fold amount of $ClSO_3F$.



The reaction proceeded as written in 95.5% yield and therefore no stable iodine (III) species was isolated, in sharp contrast to the previously mentioned $i-C_3F_7I$ case. An infrared spectrum of $n-C_3F_7SO_3F$, a new fluorosulfate, is given in Fig. 6. The mass spectrum of the compound showed no parent ion, which is often the case with perfluorinated fluorosulfates. Intense ion peaks were observed, attributable to the ions $C_3F_7^+$, $CF_2SO_3F^+$, $C_2F_5^+$, $C_2F_4^+$, SO_2F^+ , CF_3^+ (base), SO_2F^+ , SO_2F^+ , SO_2F^+ , and CF_3O^+ , all of which would be expected to arise from a compound of this type. Vapor pressure-temperature data were measured and the relationship was calculated ($\log P_{mm} = 7.4402 - 1488.3/T^\circ K$ for the temperature range, -32 to 23 C). The extrapolated boiling point is 53 C; the heat of vaporization is 6.8 kcal/mole; and the Trouton constant is 20.9. Other iodo compounds were not investigated in this regard although it would be interesting to see if another secondary iodide forms a stable iodine (III) salt.

FLUOROCARBON IODIDE-CHLORINE NITRATE REACTION

In addition to these oxidized, rearranged ionic products, it should be remembered that with SF_5OCl , the oxidized but non-ionic fluorinated



1800

1500

1200

900

600

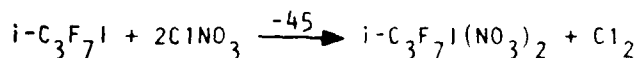
WAVENUMBER (cm⁻¹)

n-C₃F₇SO₃F (10 mm)

Figure 6. n-C₃F₇SO₃F

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product, $i\text{-C}_3\text{F}_7\text{IF}_2$, was formed. This diverse behavior made it of interest to determine where the mild oxidizing agent, chlorine nitrate, would fit in this system. The observed reaction was:



The white solid formed is an iodine III species and is not ionic. It is stable even as a melt (melting point 64 C). In simple terms, this reaction is a straightforward oxidation of iodine not involving rearrangement of any sort. However, the stability of the product is unusual compared to other $\text{R}_f\text{I}(\text{NO}_3)_2$ compounds (Ref. 16).

Table 4 lists infrared and Raman bands of this compound, together with those of $(\text{CH}_3)_4\text{NI}(\text{NO}_3)_4$ (Ref. 17), and $\text{Sn}(\text{NO}_3)_4$ (Ref. 18). There are, of course, similarities between these spectra but also significant differences. The tin compound is known to contain bidentate NO_3 groups but the iodine tetranitrate example has not been characterized sufficiently to determine whether mono- or bi-dentate NO_3 is present. Iodine trinitrate, $\text{I}(\text{NO}_3)_3$, has been investigated but its spectrum is complex and apparently indicative of a polymeric species (Ref. 19). The thermal stability of $i\text{-C}_3\text{F}_7\text{I}(\text{NO}_3)_2$ may be due to bidentate nitrate ligands being present because monodentate NO_3 is not normally so stable in this type environment.

DECARBOXYLATION REACTIONS

With carboxylic acids, acid salts, and anhydrides, the reaction of chlorine or bromine fluorosulfate at ambient temperature or slightly above was found to be a most facile decarboxylating agent.

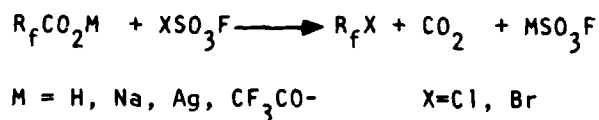


TABLE 4. INFRARED AND RAMAN SPECTRA (cm^{-1}) OF IODINE AND TIN

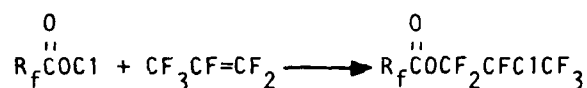
$\text{i-C}_3\text{F}_7\text{I}(\text{NO}_3)_2$		$(\text{CH}_3)_4\text{NI}(\text{NO}_3)_4^a$	$\text{Sn}(\text{NO}_3)_4$	
Ir	Raman	Ir	Ir	Raman
				1657 s
1610 s	1610 w		1622 vs	1618 s
1557 s	1570 w	1499 s	1556 m	
1417 w		1319 w		
1280 s,br	1280 w	1290 sh	1240 s	1228 w
1240 s,br	1245 w	1252 vs	1202 m	
1173 s			1170 m	
1138 s	1148 w			994 m
957 s,br	958 w	971 ms	978 s	989 m
878 s,br	885 wm		802 s	808 m
773 s	756 m	784 m	783 s	
774 s	735 m			
711 s	720 wm	725 m		
700 s	708 m	699 m	696 m	
658 s	665 vw			
615 w				
533 s	542 w			
457 vw	465 w			
	327 vs		344 vs	
	295 w			302 m
	277 w			
	240 s			247 vw
	218 w			
	182 m			
	159 w			
	145 m			
	88 w			98 m

^a Bands assigned to the $(\text{CH}_3)_4\text{N}^+$ ion were deleted.

Numerous examples were investigated. High yields were realized and, in fact, some moderation would appear warranted in some cases in order to reduce the sometimes observed secondary reaction leading to R_fSO_3F . These results are included in detail as part of Appendix D.

FORMATION OF ACYL HYPOCHLORITES AND FLUOROCARBON ESTERS

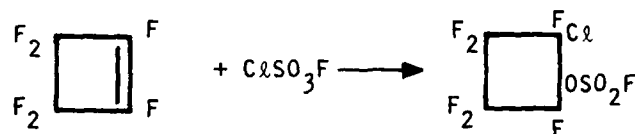
Chlorine fluorosulfate reacted with the above-mentioned substrates at low temperature to form isolable intermediate fluoroacyl hypochlorites. These novel reactive compounds, synthesized from $ClSO_3F$ for the first time on this program, were also shown to participate in typical positive halogen addition reactions with olefins leading to novel syntheses of fluorocarbon esters.



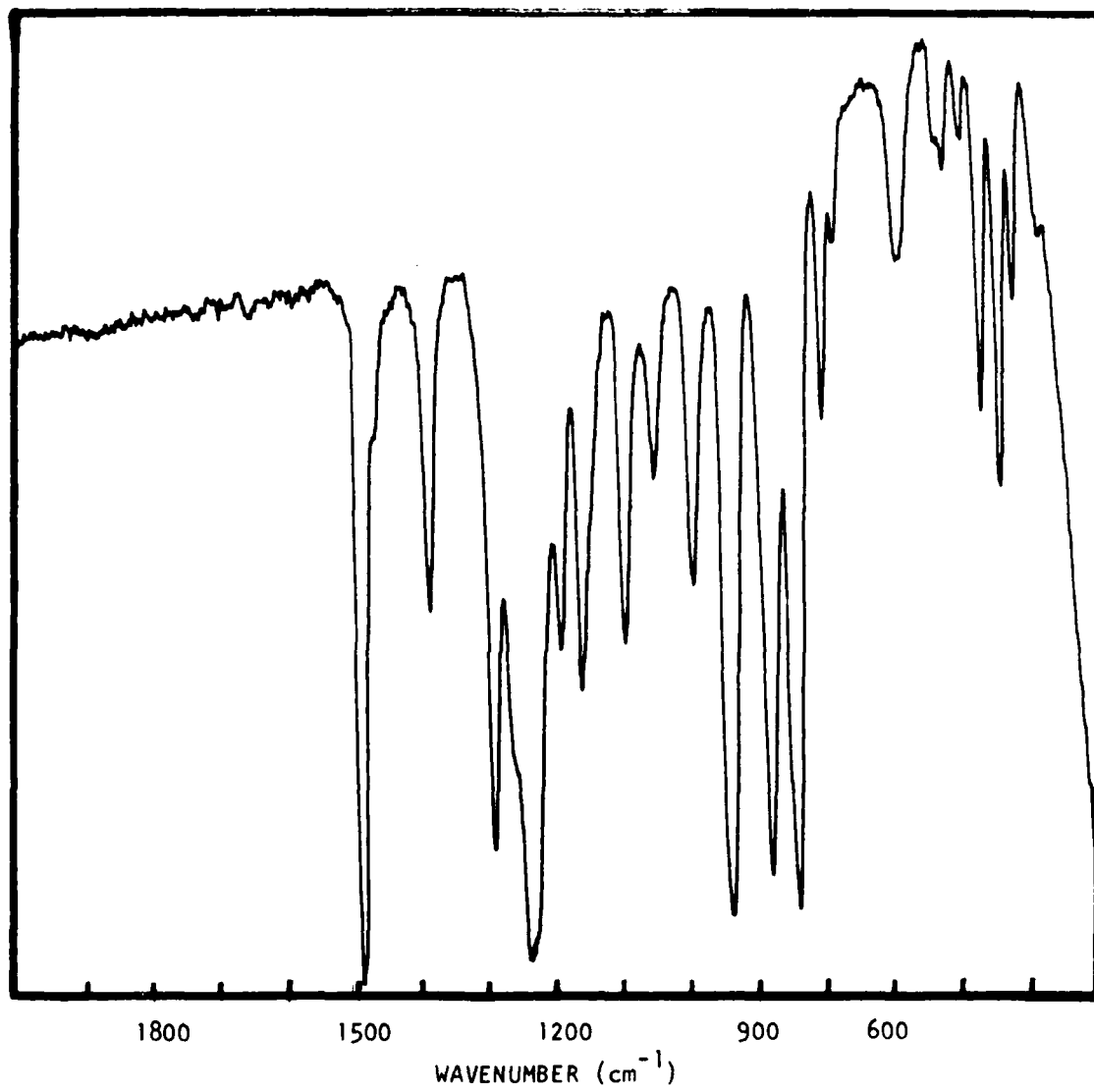
This work has been described in Appendix B.

ADDITION REACTIONS OF HALOGEN FLUOROSULFATES

Another example for the addition of $ClSO_3F$ to double bonds is its reaction with perfluorocyclobutene.



This reaction occurred in 95+ % yield to give the clear, colorless liquid fluorosulfate derivative. An infrared spectrum (Fig. 7) of the product readily shows the absorptions of the SO_3F group (1500 and $850-900\text{ cm}^{-1}$) and lack of unsaturation in the ring. Furthermore the mass spectrum of the adduct had a weak, but detectable, parent ion, m/e 298 and 296 for the chlorine isotopes. Many important ion fragments were observed and



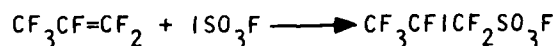
$\text{c-C}_4\text{F}_6\text{Cl}(\text{SO}_3\text{F})$ (10 mm)

Figure 7. $\text{c-C}_4\text{F}_6\text{Cl}(\text{SO}_3\text{F})$

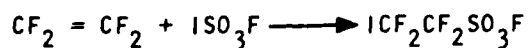
were attributable to: $C_4F_6ClO^+$, $C_4F_6Cl^+$, $C_4F_6^+$, $C_4F_5O^+$, and numerous others with CF_3^+ being the most intense. The ease with which this reaction occurred is in marked contrast to the ISO_3F case where no reaction occurred at all (see below). Perhaps this is due to the steric effect of the large iodine but it may be simply caused by the lower reactivity and oxidizing character of iodine fluorosulfate compared to chlorine fluorosulfate. The cyclobutane derivative might be subject to a ring opening reaction and as a 1, 2 hetero-substituted cyclobutane; there is also the possibility of cis or trans addition having occurred. These aspects of its chemistry were not investigated.

ADDITION REACTIONS OF IODINE FLUOROSULFATE

Iodine fluorosulfate has been known for some time (Ref. 20), but there have been almost no reports of its reaction chemistry and none at all involving organic species. Because incorporation of iodine and a fluorosulfate group into an organic compound would generate two potentially reactive sites for further manipulation, it was decided to investigate the addition of ISO_3F to fluorocarbon olefins. With hexafluoropropylene, a facile 1:1 addition reaction was found



Only one isomer was formed in an apparent directed polar addition. This agrees with similar unpublished results obtained with $ClSO_3F$ in these laboratories and elsewhere (Ref. 21). For comparison, the infrared spectra of the $CF_3CFXCF_2SO_3F$, $X=Cl$ or I , compounds are given in Fig. 8 and 9. In addition to the strong SO_3F group vibrations, it is interesting to note the apparent splitting of the C-C stretching mode at about 900 cm^{-1} which may be indicative of some hindered rotation about the carbon-carbon bond, owing to the bulky iodo substituent. In a similar manner, the addition of ISO_3F to other olefins was demonstrated.



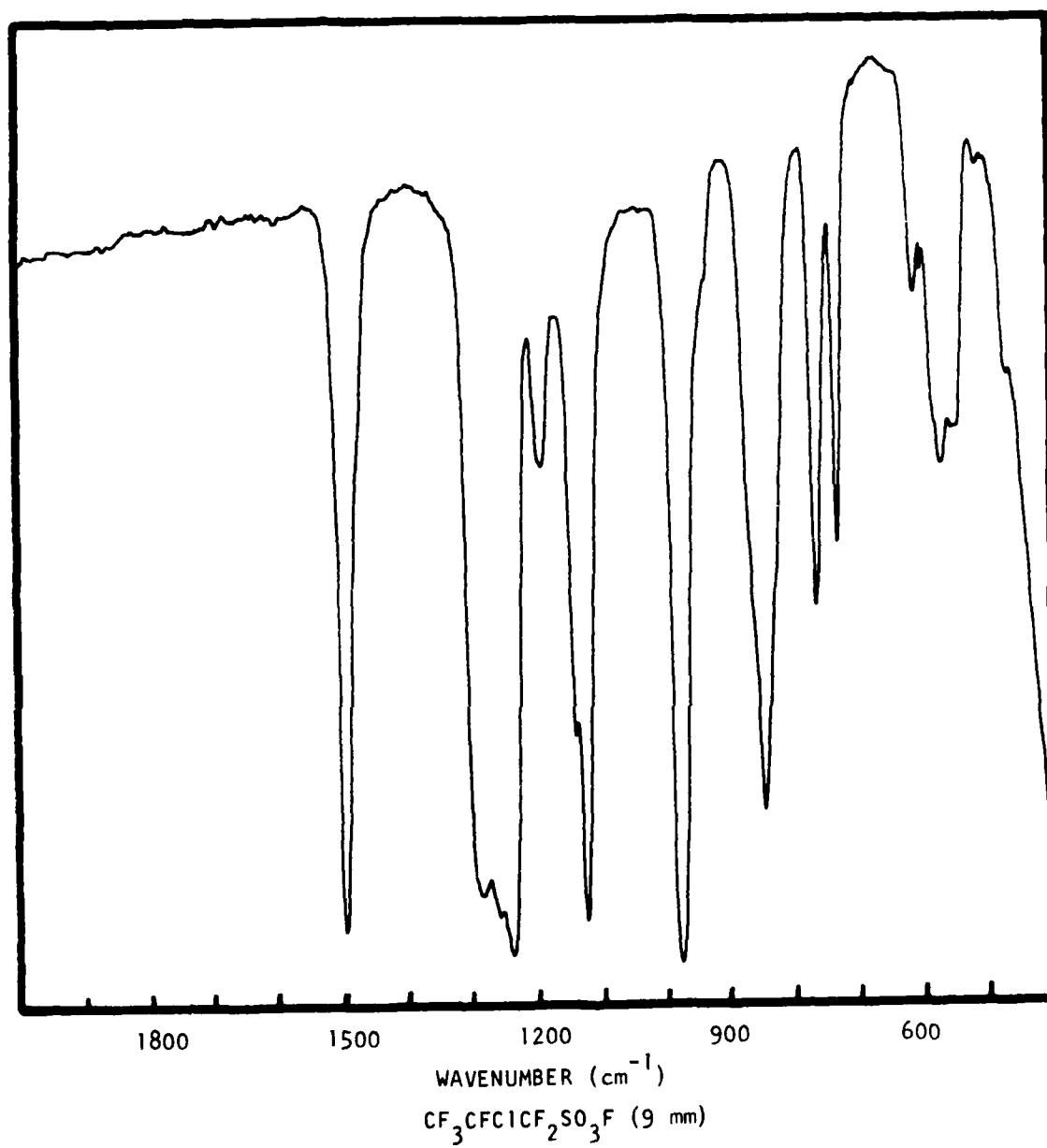


Figure 8. $\text{CF}_3\text{CFC1CF}_2\text{SO}_3\text{F}$

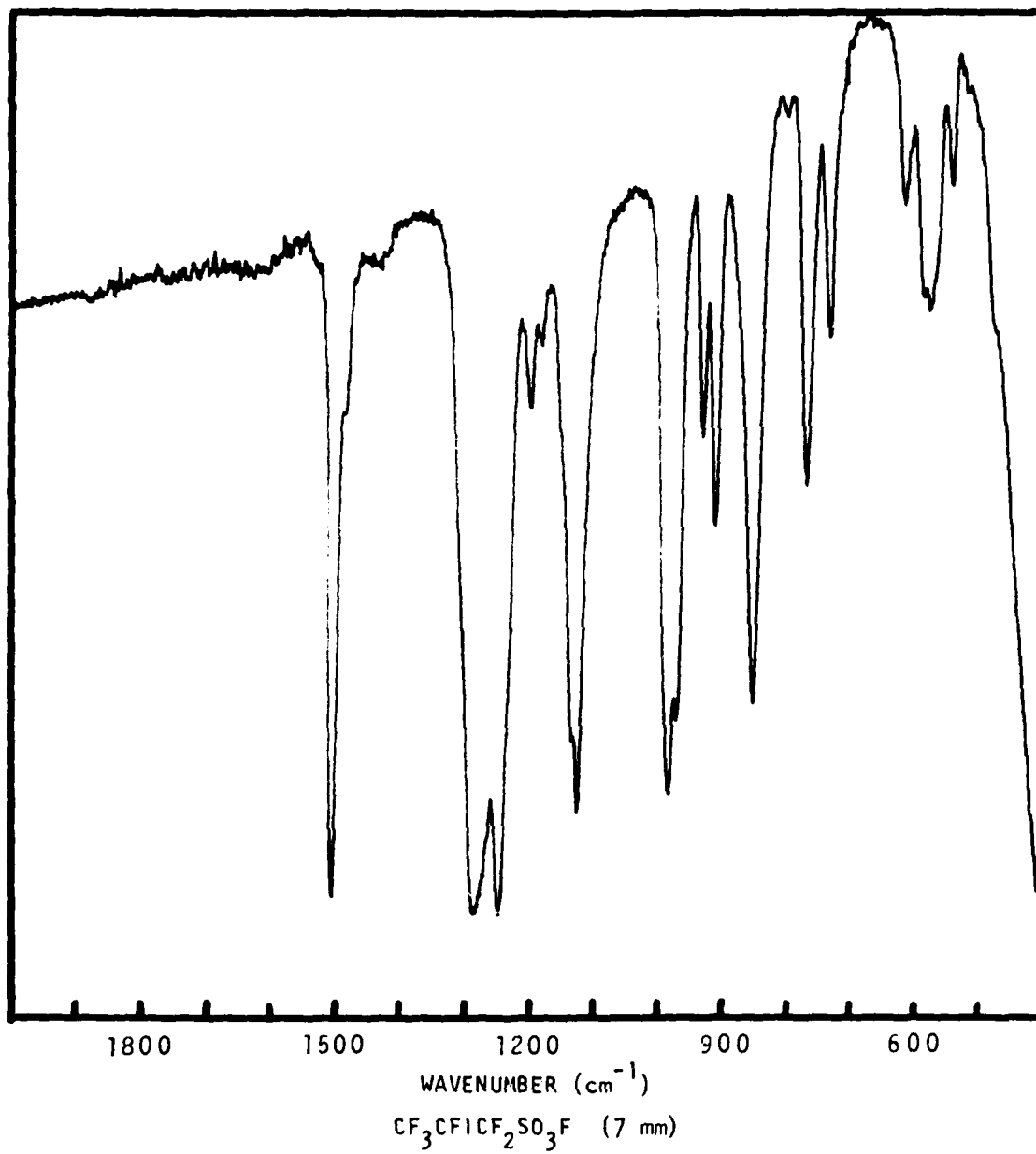
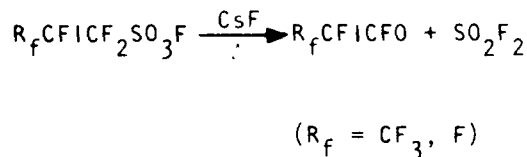


Figure 9. $\text{CF}_3\text{CFICF}_2\text{SO}_3\text{F}$

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The observed order of reactivity for the three olefins was $C_2F_4 > C_3F_6 > C_2F_3Cl$ with the tetrafluoroethylene reaction showing some tendency to be quite vigorous, resulting in polymer formation. Under the same ambient temperature conditions, perfluorocyclobutene did not react with ISO_3F . From $CF_2=CFCI$, two isomers were obtained, as indicated above. Whereas the infrared spectra (Fig. 10 and 11) are not very useful for identification of the isomers, their presence is clearly shown by mass spectroscopy and ^{19}F NMR studies.

The following high yield, derivative forming reactions were demonstrated.

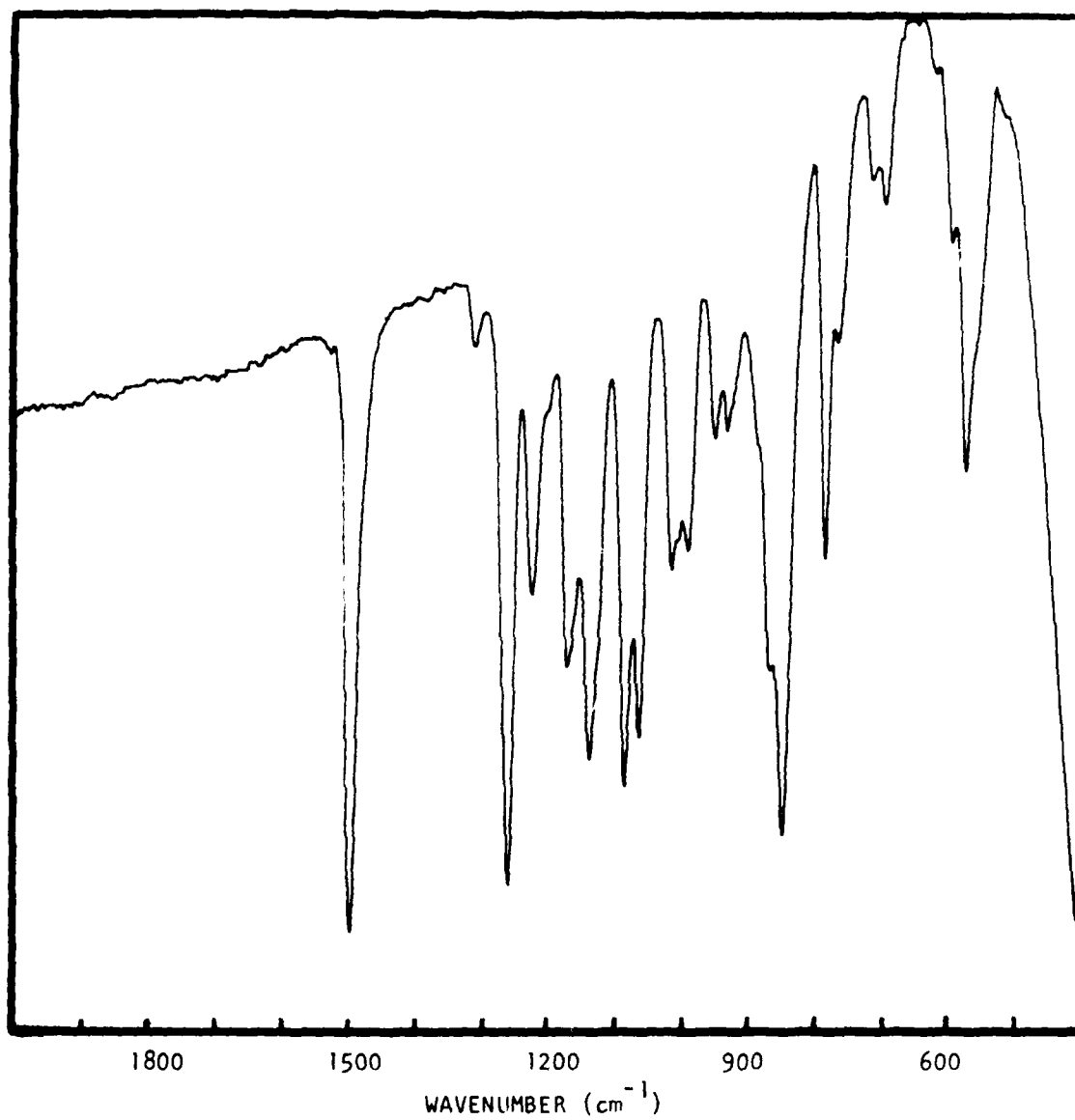


The acyl fluoride function thus obtained is a reactive end group with well documented chemistry (Ref. 22). Infrared spectra of these fluorocarbon acyl fluorides are presented in Fig. 12 to 14. The iodo substituent is not affected during the reaction of the SO_3F group and constitutes a useful second reaction site. Therefore, ISO_3F addition to olefins is an excellent method of generating bifunctional reactants containing two groups of different reactivity.

Another reaction of iodine fluorosulfate that was examined was its interaction with trifluoroacetic anhydride. The desired path was:

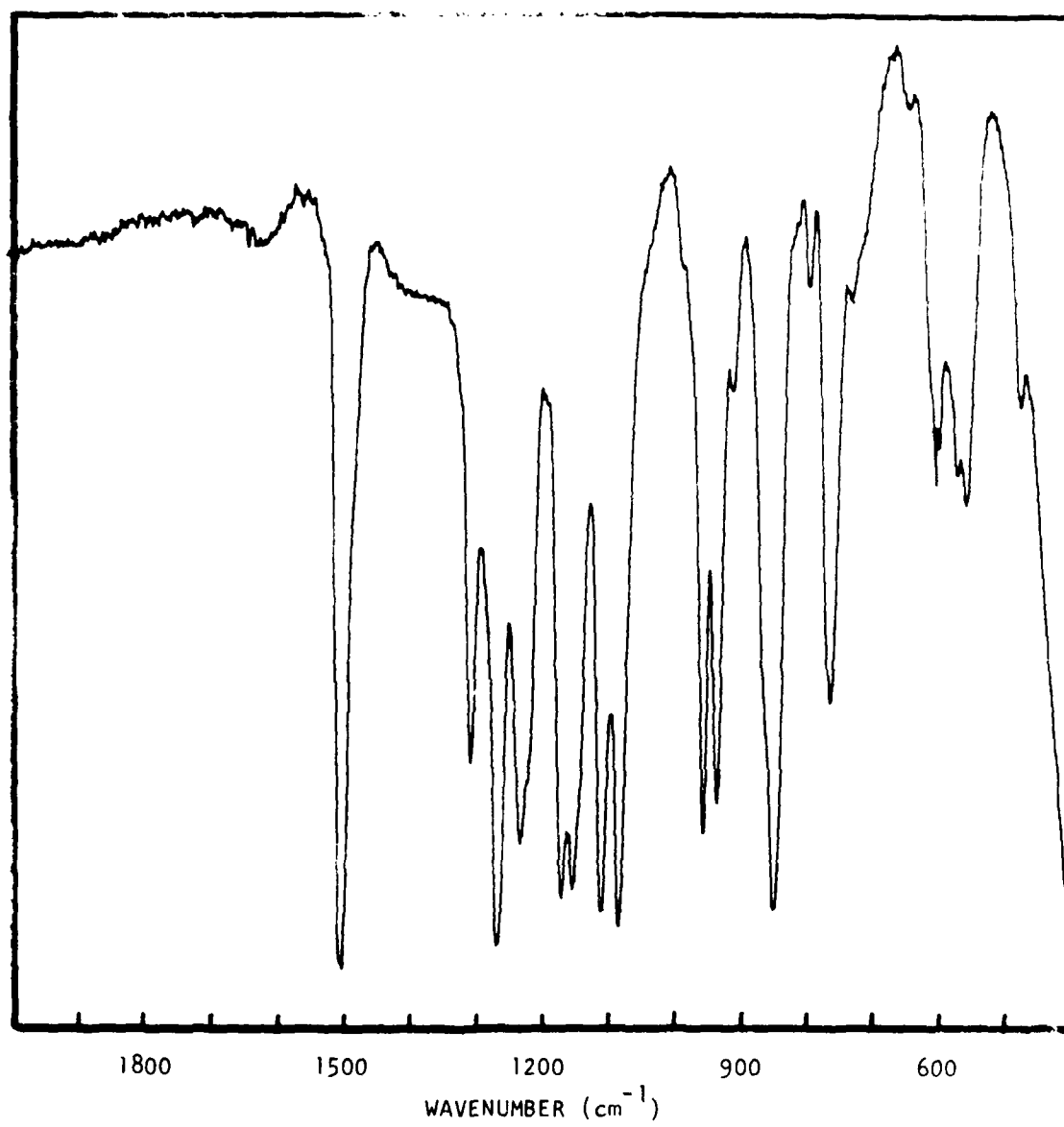


Fluorocarbon hypiodites are unknown other than as unstable intermediates. At $-20^\circ C$ no reaction occurred, while at room temperature considerable amounts of the expected byproduct, CF_3COSO_3F , were obtained. These were



$\text{ICFCICF}_2\text{SO}_3\text{F}/\text{ICF}_2\text{CFCISO}_3\text{F}$ (6 mm)

Figure 10. $\text{ICF}_2\text{CFCISO}_3\text{F}/\text{ICFCICF}_2\text{SO}_3\text{F}$



$\text{ICF}_2\text{CF}_2\text{SO}_3\text{F}$ (9 mm)

Figure 11. $\text{ICF}_2\text{CF}_2\text{SO}_3\text{F}$

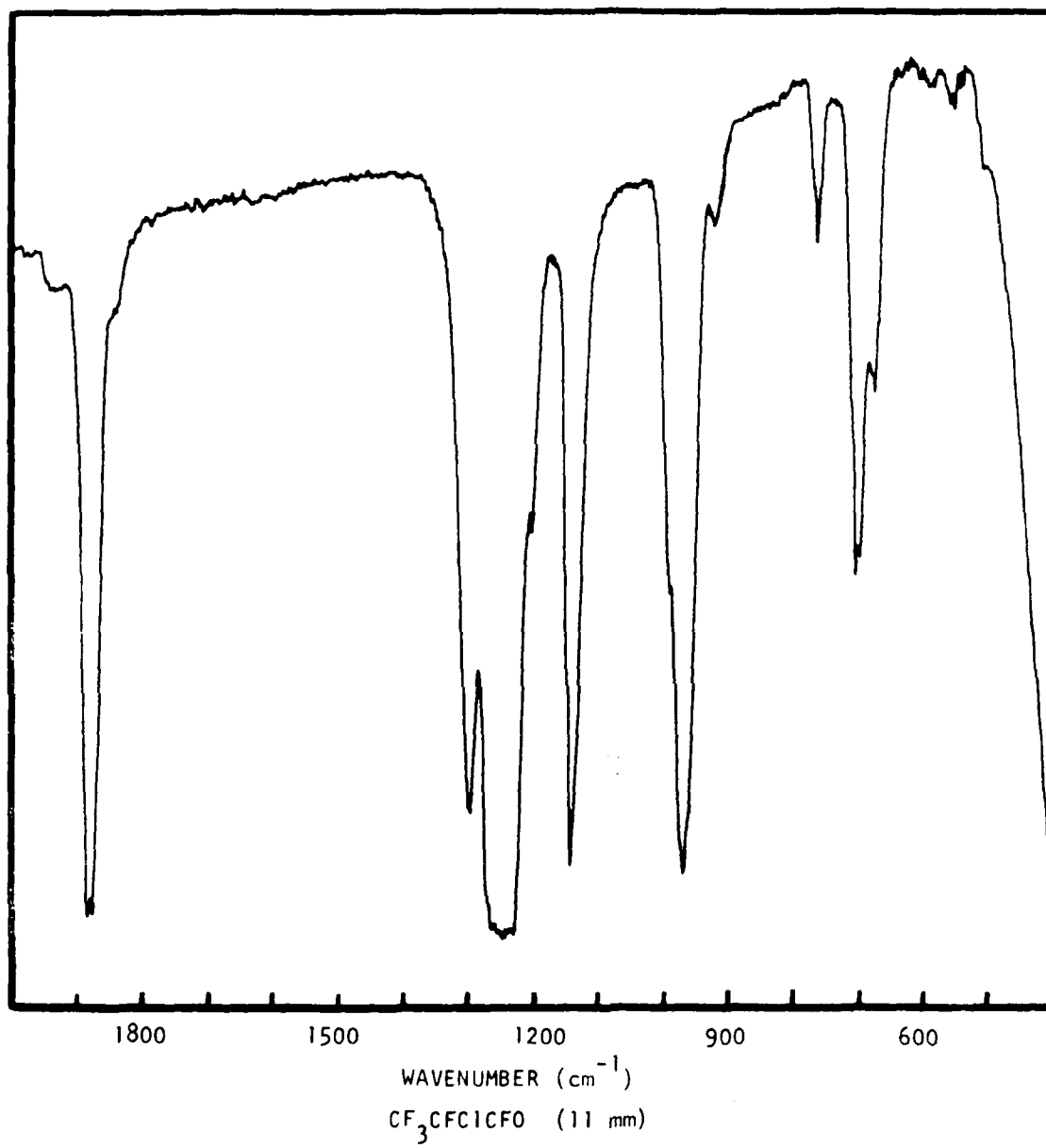


Figure 12. $\text{CF}_3\text{CFC1CFO}$

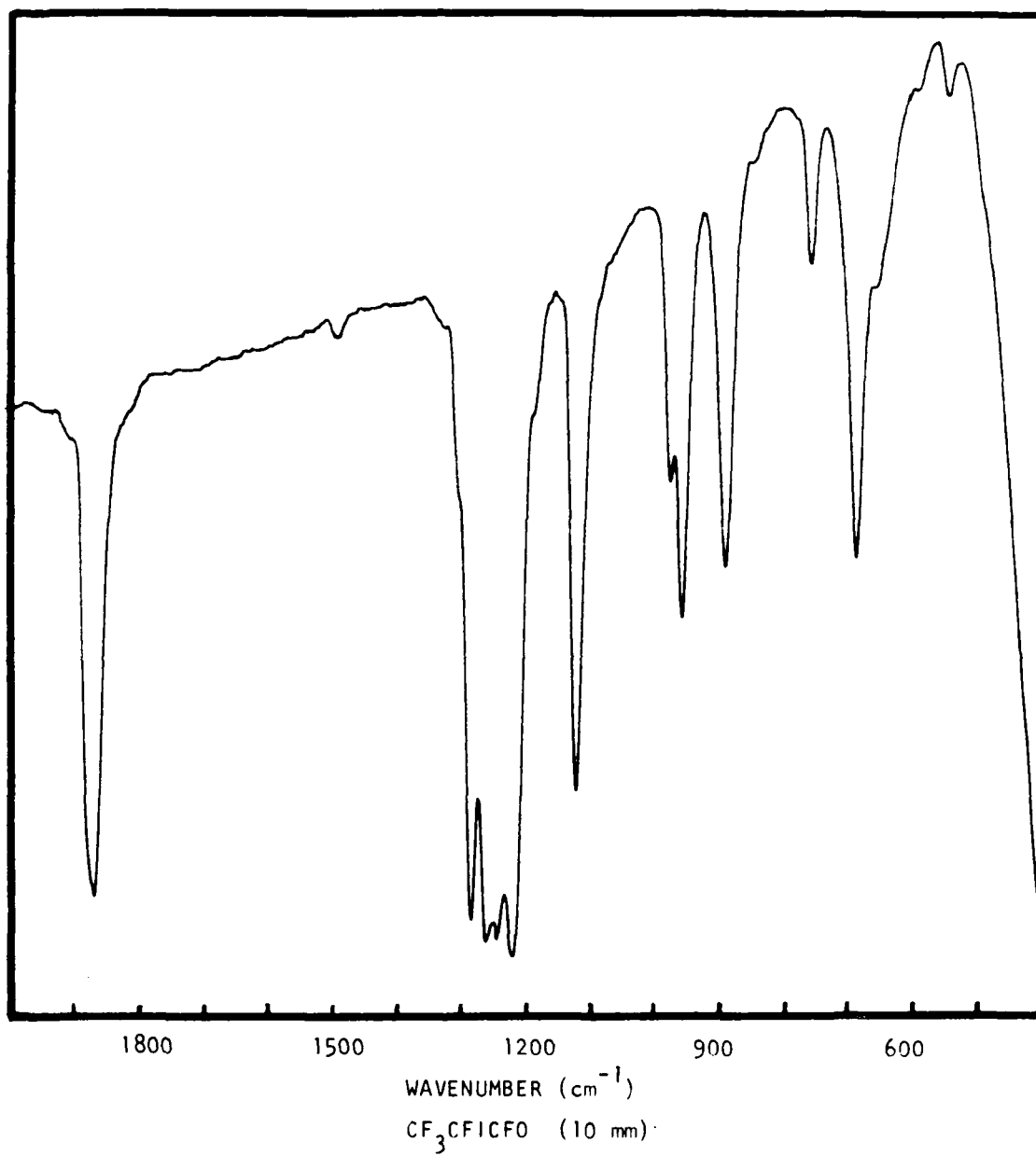


Figure 13. CF3CFICFO

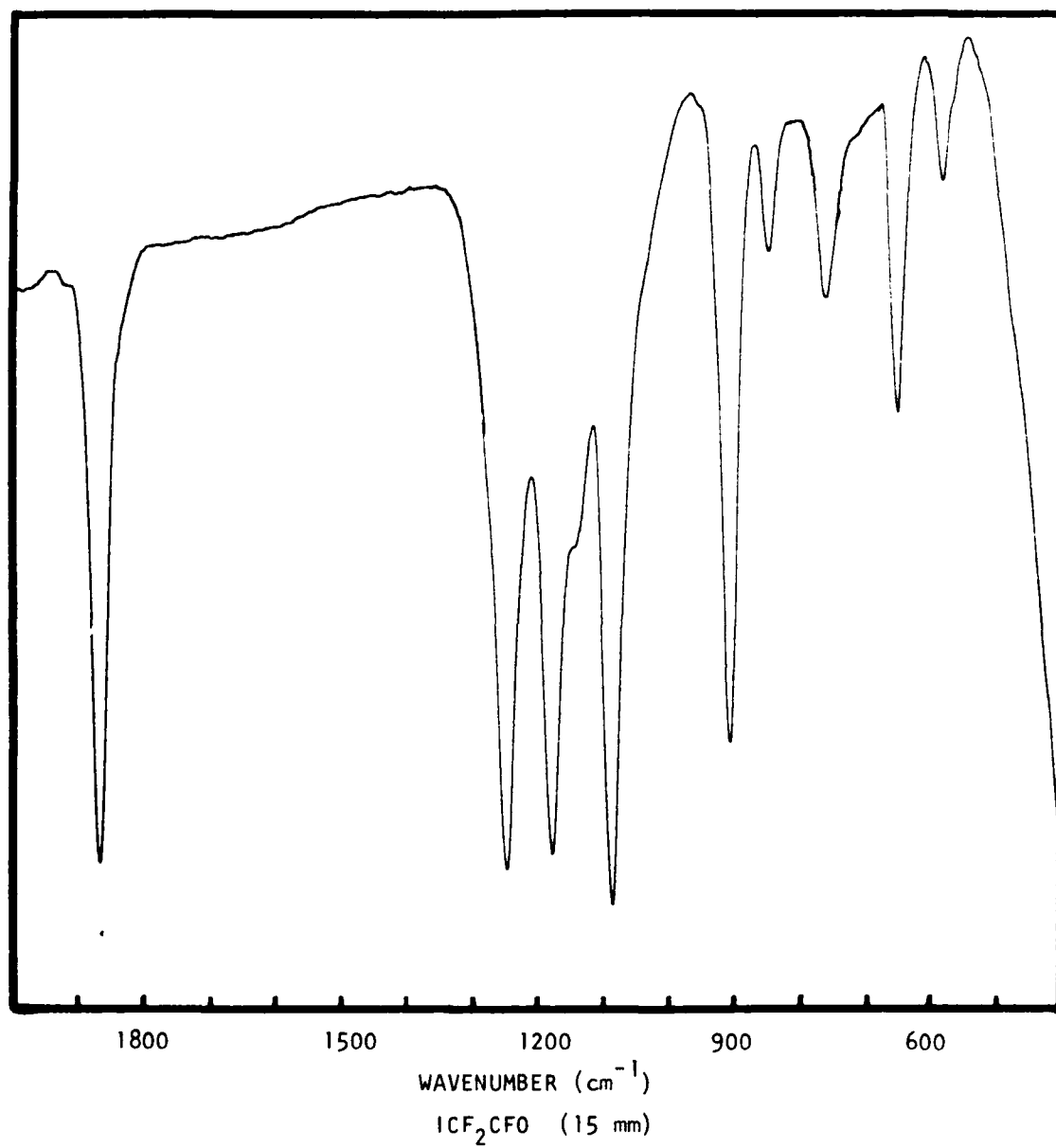
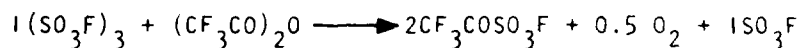
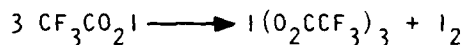


Figure 14. ICF₂CFO

accompanied by significant portions of CF_3CFO , but by no other volatile species except for unreacted anhydride. If the hypoiodite had formed and decomposed, both CF_3I and CO_2 would have been expected. In part, the $\text{CF}_3\text{COSO}_3\text{F}$ could have arisen from reaction with impurity $\text{I}(\text{SO}_3\text{F})_3$.



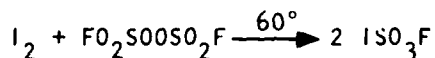
However, the amount of $\text{CF}_3\text{COSO}_3\text{F}$ obtained was too great to be accounted for wholly by that reaction. Any disproportionation reaction of the hypoiodite should result in I_2 formation and this would have been readily apparent.



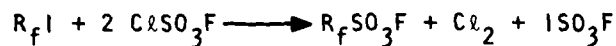
Thus the iodine species produced was not ascertained for this system and time did not permit further investigation. Nevertheless, it was verified that ISO_3F was still present even after the $(\text{CF}_3\text{CO})_2\text{O}$ interaction, by adding hexafluoropropylene to the reactor and observing the formation of $\text{CF}_3\text{CFICF}_2\text{SO}_3\text{F}$.

Iodine Fluorosulfate Preparation

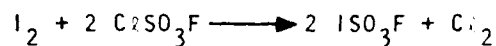
Before concluding this discussion of iodine fluorosulfate reactions, it should be noted that two new routes for the preparation of that compound were developed on this program. The literature procedure (Ref. 20) used the peroxide as shown in the equation.



The first method used in our study was simply to use the byproduct from our $\text{R}_f\text{I}-\text{ClSO}_3\text{F}$ displacement reactions.



Iodine fluorosulfate that had been formed in this reaction and had been stored at room temperature for nearly 2 years was unchanged and still suitable for addition reactions with olefins. Second, it was found that the I_2-ClSO_3F reaction also furnishes iodine fluorosulfate at temperatures near $-45^\circ C$.



This reaction makes more efficient use of starting materials. However, care must be exercised to avoid further oxidation of iodine to the +3 iodine fluorosulfate which can form when using too high a temperature or more than stoichiometric amounts of $ClSO_3F$. Details concerning iodine fluorosulfate and its reactions with olefins are contained in Appendix E.

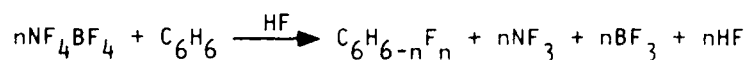
FLUORINATION REACTIONS

The known methods for introducing fluorine into an aromatic ring are quite limited and are often not generally applicable (Refs. 22 to 25). A widely applicable reagent for carrying out substitution reactions on aromatic systems would therefore be highly desirable. The potential NF_4^+ salts in this regard seemed promising and were studied. Hydrogen fluoride was used as a solvent because of the high solubility of NF_4^+ salts in it, and because the diluent and heat dissipation properties of solvated systems were expected to be beneficial in the anticipated vigorous fluorination.

Numerous NF_4^+ salts have been prepared at Rocketdyne, mostly by metathetical reactions (Refs. 26, 27) and some in multi-kilogram quantities; consequently, these salts are readily available and are not just laboratory curiosities. NF_4BF_4 was selected for the present work because it can be prepared in pure form by the low temperature uv photolysis of $NF_3-F_2-BF_3$ mixtures (Ref. 28), and because the counter-ion, BF_4^- , was expected to be noninterfering in the projected study.

Fluorination of Aromatic Hydrocarbons

In one of our previous reports (Ref. 29), the reaction of benzene with NF_4BF_4 in HF was described. These reactions were carried out by either adding benzene vapor to a cooled solution of NF_4BF_4 in HF or by slowly adding a solution of NF_4BF_4 to a solution of benzene in HF. Gas evolution was noted on contact. When the addition was too rapid, some apparent charring occurred. The stepwise substitution of H by F was observed according to the general equation:



where $n=1-5$

The mass spectra of the volatile products (Table 5) illustrate the degree of fluorination. Because the parent ion, C_6F_6^+ , is the base peak in the mass spectrum of hexafluorobenzene (Ref. 30), its absence is definitive evidence for the lack of that compound in the product mixture. The few ions attributable to partially saturated species were of low intensity. Unreacted benzene was the principal material present in this sample. The fact that C_6F_6 was not produced, and little ring addition occurred, indicates that this fluorination scheme may have special utility in generating aromatic fluorocarbons from their hydrocarbon analogues while leaving select functions unaffected.

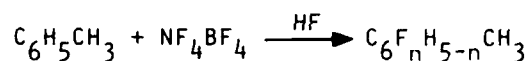
Because the selective introduction of fluorine into aromatic rings is of great interest for the preparation of important fluorinated drugs and steroids, as well as for the production of highly fluorinated fluids and monomers, two aromatic compounds which had substituents already on the ring were investigated. These were toluene and nitrobenzene. They were chosen because of their well-known dissimilar activating effects in aromatic substitution processes. Because the methyl group is electron donating and the nitro group is electron withdrawing it was anticipated

TABLE 5. MASS SPECTRUM OF BENZENE - NF_4BF_4 REACTION PRODUCTS

m/e	assign.	m/e	assign.	m/e	assign.
206	$\text{C}_6\text{F}_7\text{H}^+$	115	$\text{C}_6\text{F}_2\text{H}_5^+$	70	C_4FH_3^+
		114	$\text{C}_6\text{F}_2\text{H}_4^+$	69	C_4FH_2^+
188	$\text{C}_6\text{F}_6\text{H}_2^+$	113	$\text{C}_6\text{F}_2\text{H}_3^+$	68	C_4FH^+
187	$\text{C}_6\text{F}_6\text{H}^+$	112	$\text{C}_6\text{F}_2\text{H}_2^+$		
				64	C_5H_4^+
168	$\text{C}_6\text{F}_5\text{H}^+$	101	$\text{C}_5\text{F}_2\text{H}_3^+$	63	C_5H_3^+
167	C_6F_5^+	100	$\text{C}_5\text{F}_2\text{H}_2^+$	62	C_5H_2^+
		99	$\text{C}_5\text{F}_2\text{H}^+$	61	C_5H^+
150	$\text{C}_6\text{F}_4\text{H}_2^+$				
149	$\text{C}_6\text{F}_4\text{H}^+$	96	C_6FH_5^+	57	C_3FH_2^+
		95	C_6FH_4^+		
143	C_4F_5^+	94	C_6FH_3^+	52	C_4H_4^+
		93	C_6FH_2^+	51	C_4H_3^+
138	$\text{C}_5\text{F}_4\text{H}_2^+$	92	C_6FH^+	50	C_4H_2^+
137	$\text{C}_5\text{F}_4\text{H}^+$			49	C_4H^+
136	C_5F_4^+	88	$\text{C}_4\text{F}_2\text{H}_2^+$		
				40	Ar^+
132	$\text{C}_6\text{F}_3\text{H}_3^+$	81	C_5FH_2^+	39	C_3H_3^+
		79	C_5F^+	38	C_3H_3^+
126	$\text{C}_4\text{F}_4\text{H}_2^+$			37	C_3H^+
119	$\text{C}_5\text{F}_3\text{H}_2^+$	78	C_6H_6^+		
		77	C_6H_5^+		
		76	C_6H_4^+		
		75	C_6H_3^+		
		74	C_6H_2^+		

that the ortho-meta-para product distribution would allow one to distinguish between an electrophilic and a free radical reaction path.

When toluene vapor was added to a stirred solution of NF_4BF_4 in HF at -78°C , immediate gas evolution (NF_3) occurred and was accompanied by darkening of the solution. After the addition of each increment of toluene, the reaction was complete in seconds. A similar result was observed when NF_4BF_4 in HF was added to toluene in HF at -78°C . In these systems the ratio of NF_4^+ to toluene was in the range of 2-4:1. Thus, considerable amounts of fluorine were available (assuming one F/NF_4^+ is available for substitution) and multisubstitution was expected. After removal of the HF, BF_3 , and volatile components that passed a -78°C trap, the fluorinated products were examined. By infrared spectroscopy, retention of the aromatic character of the ring was established. Mass spectroscopy showed that fluoroaromatic toluenes were present with up to four fluorines per ring.



where $n=1-4$

It is important to note that no evidence was obtained for side chain fluorination. Table 6 shows the mass spectrum of a typical product fraction. The low relative intensity of m/e 69 and 51, for example, strongly indicates that CF_3 and CF_2H groups are not present in the parent compound. There are m/e values assignable to de-methylated products, e.g., $\text{C}_6\text{F}_2\text{H}_4$ and C_6FH_5 , however, these might also be recombination ions or even ions which have lost one ring carbon while retaining the methyl carbon thereby giving the appearance, based on the C-F-H ratio, of being benzenes.

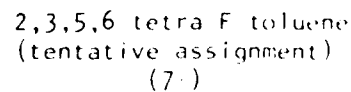
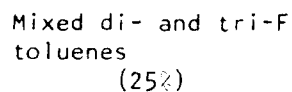
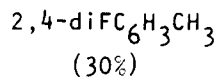
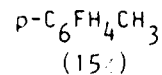
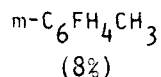
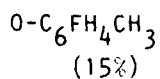
TABLE 6. MASS SPECTRA OF TOLUENE-NF₄BF₄ REACTION PRODUCTS^a

<u>m/e Intensity</u> <u>(assigned)</u>			<u>m/e Intensity</u> <u>(assigned)</u>		
164	11	C ₇ F ₄ H ₄ ^b	96	6	C ₆ FH ₅
163	13	C ₇ F ₄ H ₃	83	12	C ₅ FH ₄
146	44	C ₇ F ₃ H ₅ ^b	81	12	C ₆ FH ₂
145	70	C ₇ F ₃ H ₄	77	6	C ₆ H ₅
128	53	C ₇ F ₂ H ₆ ^b	75	24	C ₆ H ₃
127	100	C ₇ F ₂ H ₅	69	7	C ₄ FH ₂ /CF ₃ ?
125	11	C ₇ F ₂ H ₃	63	20	C ₅ H ₃
119	4	C ₅ F ₃ H ₂	62	9	C ₅ H ₂
114	3	C ₆ F ₂ H ₄	57	34	C ₃ FH ₃
110	23	C ₇ FH ₇ ^b	51	28	C ₄ H ₃ /CF ₂ H?
109	45	C ₇ FH ₆	50	13	C ₄ H ₂
101	9	C ₆ F ₂ H ₃			

a. Positive ion spectrum, charge sign deleted.

b. Parent ions.

Examination of the NMR spectra of the products, particularly the ^{19}F NMR confirmed again that a mixture of aromatic fluoro toluenes had been formed. From the area ratios observed, a typical mixture was:



In one case, both mass spectroscopy and ^{19}F NMR indicated a small quantity of $\text{p-C}_6\text{F}_4\text{H}_2$ had been formed by loss of CH_3 during fluorination. This occurred in an experiment with a high relative amount of NF_4BF_4 . The dominance of ortho and para products for this electron-rich ring system is compatible with an electrophilic substitution process.

Nitrobenzene reacted with NF_4BF_4 (solution added to solution at -78°C) in a milder fashion than either benzene or toluene. This was indicated by a slightly slower rate of gas evolution, and the fact that the solution did not become dark until late in the reaction when it was warmed to near 0°C . This reaction was conducted using a 10:3 excess of $\text{C}_6\text{H}_5\text{NO}_2$ to NF_4BF_4 . Only very little volatile product at 0°C was found after removal of HF , NF_3 , and BF_3 . This volatile product was mainly an $\text{NO}_2\text{F}(\text{HF})_n$ complex which was observed in the mass spectrum for $n=1$. Carbon moieties in trace amounts all lacked the NO_2 substituent which, no doubt, contributed to their volatility. The carbon compounds were of empirical formula $\text{C}_6\text{F}_n\text{H}_{6-n}$, and thus aromatic. But again, they were only detected as trace materials.

The liquid product left behind at 0 C was mainly the excess $C_6H_5NO_2$ with a mixture of fluoro-nitro derivatives:

$O-C_6FH_4NO_2$ (16%)	$m-C_6FH_4NO_2$ (62%)	$p-C_6FH_4NO_2$ (7%)
2,6 or 3,5 di-F nitrobenzene (14%)	2,4 di-F nitrobenzene (~1%)	2,3,5,6 tetra-F benzene (trace)

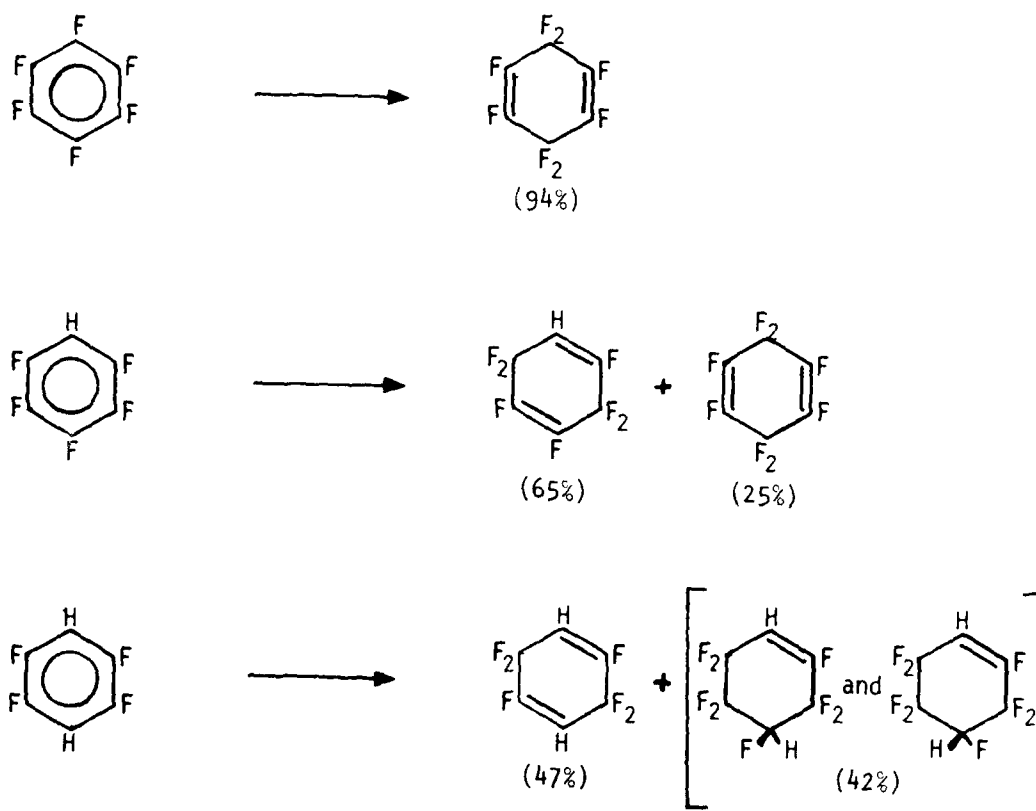
The main mono substitution product is the meta derivative, as expected for an electrophilic substitution mechanism involving a substrate containing a strongly electron withdrawing NO_2 group. This depletion of electron density in the ring also served to moderate the interaction with NF_4^+ and much less char was formed.

From these screening experiments it is readily apparent that NF_4^+ salts might be very useful reagents for the preparation of substituted fluoro-aromatics, especially when multisubstitution is desired. No evidence for addition reactions was observed, at least not until 4 to 5 fluorines had been introduced into the ring in place of hydrogen. Also, it is apparent that milder and more controlled conditions are required to fully exploit this very active reagent. More dilute solutions and lower temperatures are obvious changes to be investigated. The main point, however, is that a new method of introducing fluorine into an aromatic ring has been discovered which retains the aromatic character of the ring and may not adversely affect saturated or oxidized substituents.

Fluorination of Fluorinated Aromatics

To obtain more data on the step-by-step reaction of aromatics with NF_4^+ it was decided to examine systems which were highly fluorinated and thus more inert toward a strongly fluorinating electrophilic reagent. This was also expected to show whether the apparent tendency of these systems to stop at the tetra- or penta-fluoro stage was general.

Experiments were carried out using three different fluorobenzene starting materials. All reacted gradually at, or near, ambient temperature. The fluorine uptake by the substrates was equivalent to one F/NF_3 and the liberated NF_3 was recovered and measured. All solutions and products were colorless throughout the reactions. Excess, unreacted NF_4BF_4 was recovered and measured to confirm the observed stoichiometry of reaction. The products of these reactions were identified by infrared spectroscopy, gas chromatography-mass spectroscopy, and NMR. Because some of the products have been reported in the literature, their identification was unequivocal. The overall results are shown by the equations.



In all cases, at least 92% of the starting material was recovered as products or unreacted. The figures in parentheses are yields based on

the aromatic starting material and the balance was either not recovered or was unreacted starting compound.

It is at once noticeable that in these highly fluorinated aromatics, very little or no hydrogen substitution occurred. This confirms the results discussed above, showing that the electrophilic substitution of H by F using NF_4BF_4 is limited to almost four fluorines per ring. Beyond that point, addition of fluorine becomes the dominant reaction. The addition reactions are much slower than the substitution reactions, as shown by the fact that reaction times of 1 or 2 days were required for the addition reactions with NF_4^+ . Also, the strong tendency of these compounds to add fluorine in para positions and thus give as a first product, 1,4-dienes, appears to be general. This is often the case with fluoroaromatics but not so exclusively as here (Ref. 22, 23). The infrared spectra (Fig. 15 to 20) which follow permit a comparison of two of the starting materials with their NF_4^+ fluorination products. These spectra illustrate well the symmetry ongoing from the arene to the diene. Thus the strong aromatic ring band near 1500 cm^{-1} disappears and is replaced by the $\text{C}=\text{C}$ band near 1720 cm^{-1} .

For all of the three highly fluorinated benzenes, the addition of the first two fluorines occurs in para position to each other (1,4 addition) and ortho to any hydrogen, if present. The addition of a second pair of fluorines cannot proceed by a 1,4 mechanism without changing the ring into a bicycle form, which is generally encountered only under photolytic conditions. Thus, the second pair of fluorines undergoes a 1,2 addition to yield a cyclohexene.

For pentafluorobenzene, some substitution was also observed. At this point, we cannot say whether this is the result of a true substitution or of an addition-elimination reaction. In the case of $p\text{-C}_6\text{F}_4\text{H}_2$, the second F_2 addition produces the 1H, 4H-octafluorocyclohexene which has two possible geometric isomers. Trace quantities of the saturated product, $\text{C}_6\text{F}_{10}\text{H}_2$, were also detected by mass spectroscopy.

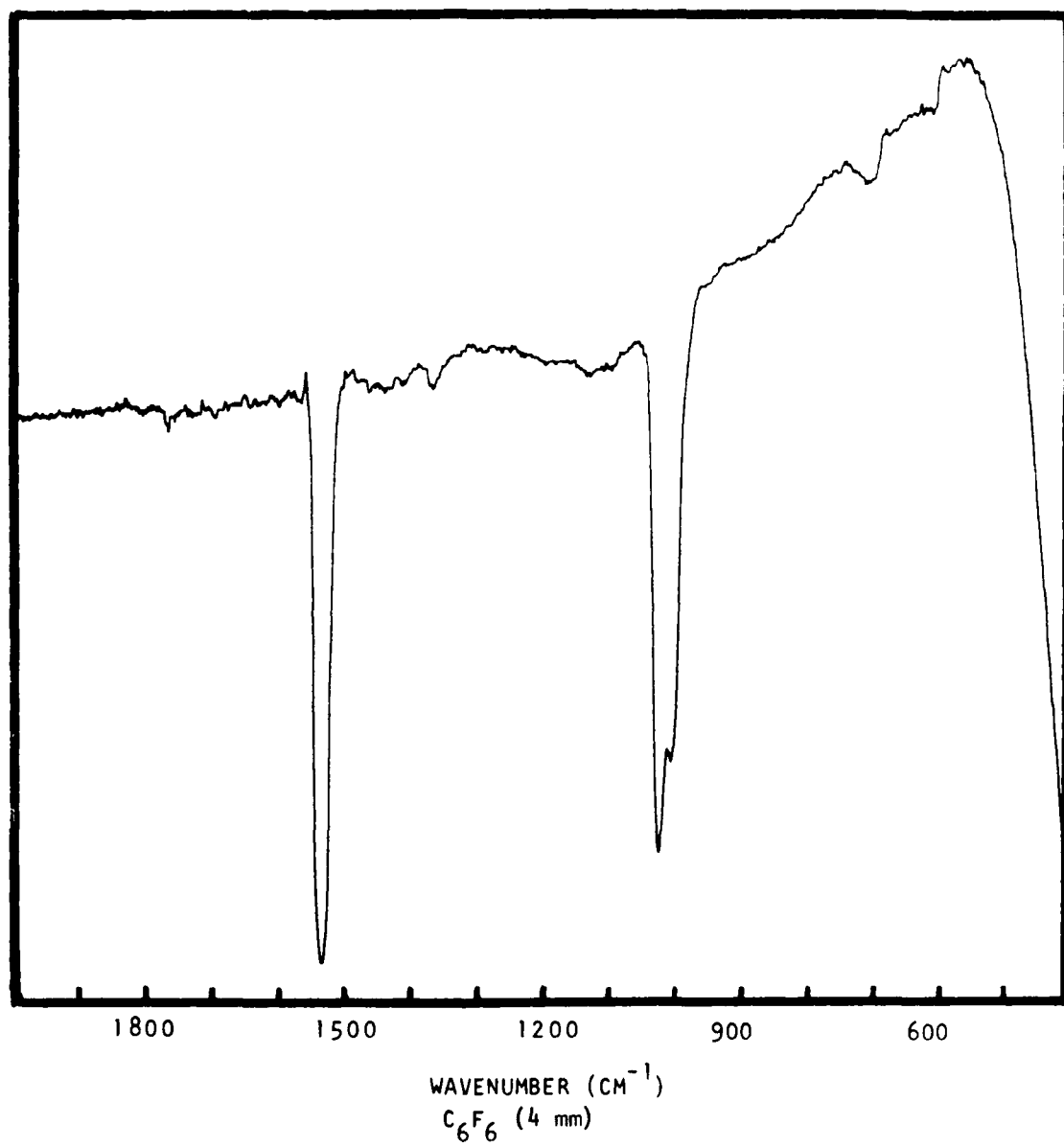
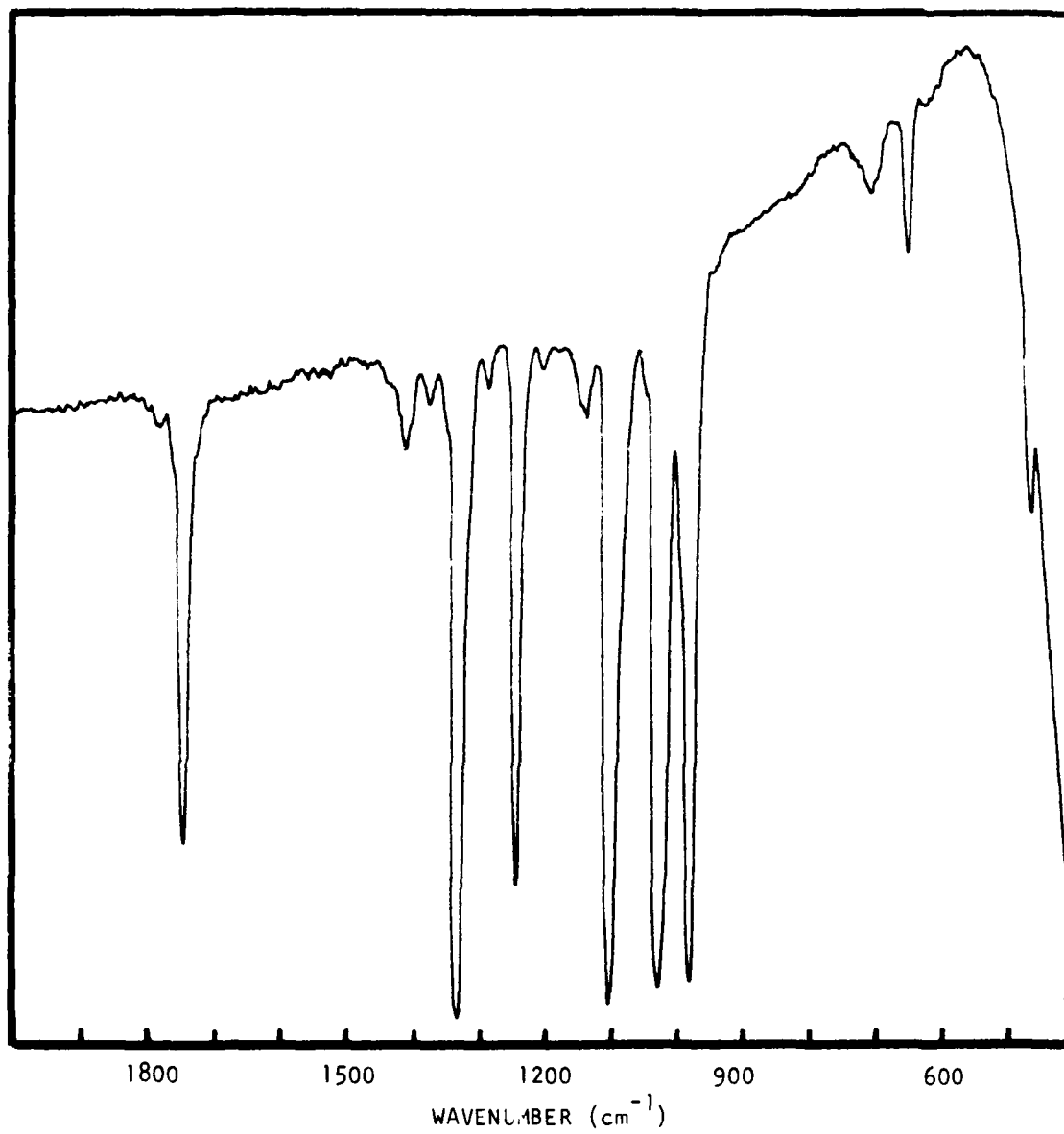


Figure 15. C_6F_6



1,4-C₆F₈ (9 mm)

Figure 16. 1,4-C₆F₈

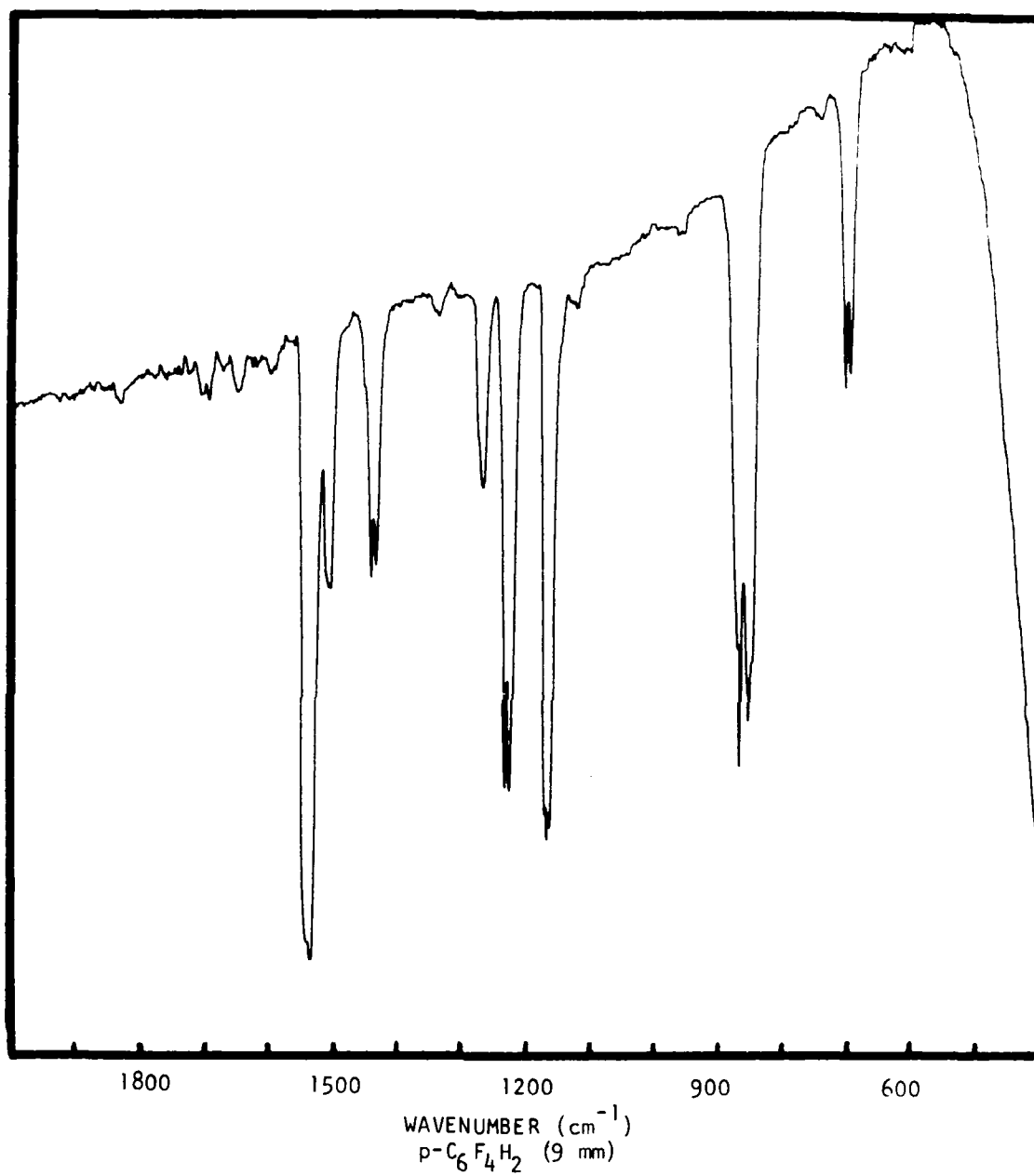
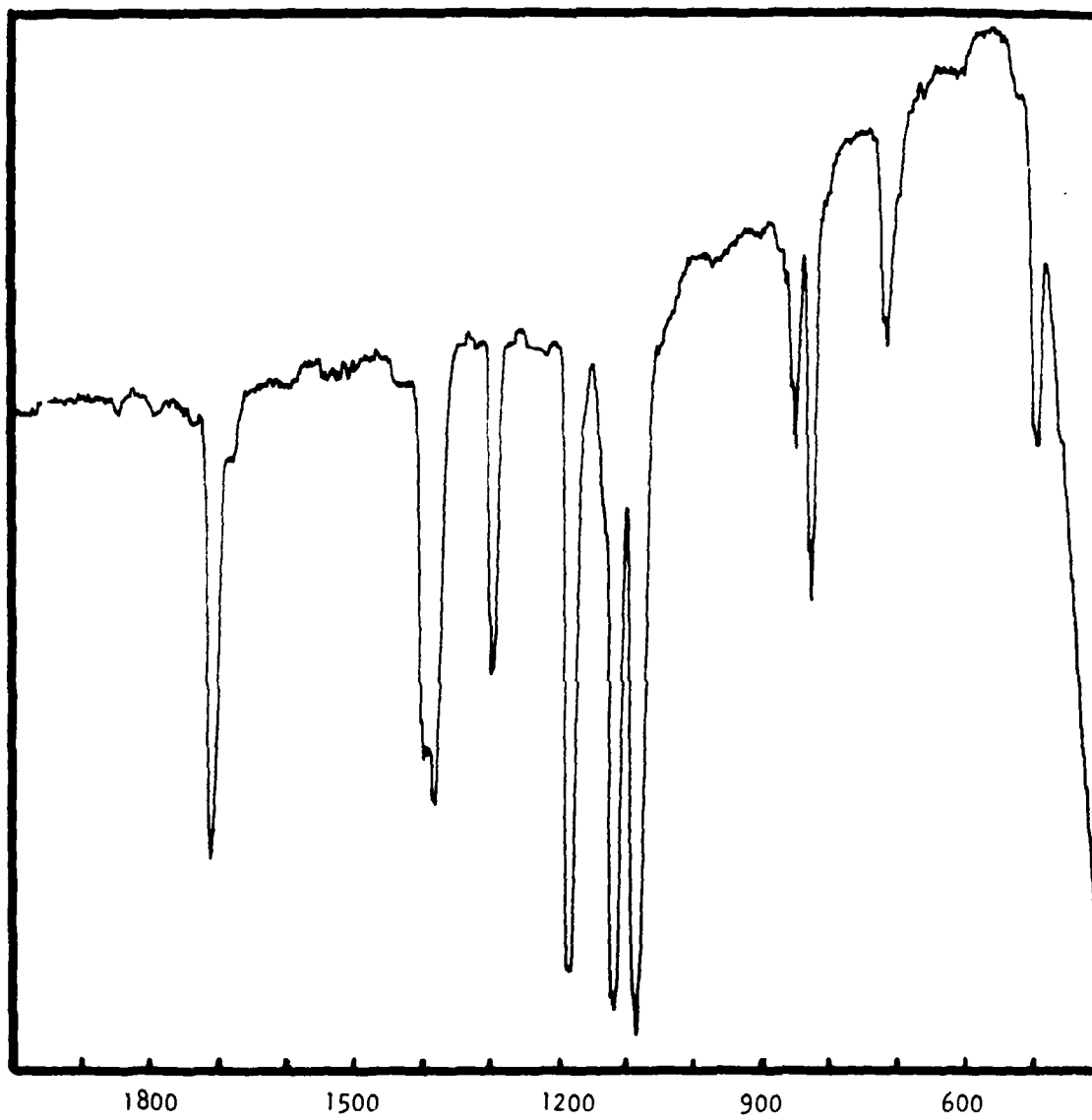


Figure 17. p-C₆F₄H₂



WAVENUMBER (cm⁻¹)

1,4-C₆F₆H₂ (7 mm)

Figure 18. 1,4-C₆F₆H₂

RI/RD 80-152

These addition reactions are novel and offer a controlled high yield path to dienes which have previously only been obtained as parts of complex mixtures (Refs. 22, 31). A more detailed discussion of the synthesis and characterization of these aromatic $-NF_4^+$ reaction products is given in Appendix F.

The chemistry of electropositive chlorine compounds has played an important part in this work and has been a long time interest of ours in both organic and inorganic applications. Because of our long involvement in this area, we were requested to prepare a review on fluorocarbon-positive chlorine chemistry by the editors of the Israel Journal of Chemistry. This review appeared in a special issue of the journal devoted to fluorine chemistry and is contained in Appendix G.

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STATUS OF THE RESEARCH EFFORT

Several different $\text{SF}_5\text{O}-$ and $\text{CF}_3\text{O}-$ fluorocarbon fluids have been prepared. Some of the simpler materials have been identified fully and characterized. Others are telomers and their purification and characterization was limited.

Chlorine and bromine fluorosulfate have been shown to be effective in displacing select halogen or hydrogen atoms in fluorocarbons by $-\text{SO}_3\text{F}$.

The scope of this $\text{R}_f\text{Hal}-\text{XS}\text{O}_3\text{F}$ reaction system was defined and summarized in manuscript form.

Functionalization and derivative formation was successfully accomplished on $\text{SF}_5\text{O}-$ and $\text{CF}_3\text{O}-$ ethers and the results were written up as a manuscript.

Decarboxylation of carboxylic compounds with ClSO_3F and BrSO_3F provided a facile route to R_fCl and R_fBr moieties.

Combining the decarboxylation and $-\text{SO}_3\text{F}$ substitution processes provides a valuable fluorocarbon chain-shortening technique.

The discovery of fluorocyl hypochlorites and their characterization and use in the synthesis of fluorocarbon esters was carried out and describe in a manuscript.

Improved synthetic procedures were developed for some sulfur fluoride and oxyfluoride peroxides, and this was published.

The discovery and characterization of several novel iodonium salts of the general formula $[(\text{R}_f)_2\text{I}]^+[\text{IX}_4]^-$ was accomplished.

The novel compounds $i\text{-C}_3\text{F}_7\text{IF}_2$ and $i\text{-C}_3\text{F}_7\text{I}(\text{NO}_3)_2$ were synthesized and shown to be covalent, the latter being very stable.

The previously unknown reaction chemistry of iodine fluorosulfate with fluorocarbons was discovered and new routes to iodine fluorosulfates were defined.

Olefin-iodine fluorosulfate derivatives were synthesized, characterized, and found to be potentially useful bifunctional species. A manuscript was written describing this work.

A new method was discovered for the introduction of from 1 to 5 fluorines in benzene rings, with retention of aromaticity, using NF_4BF_4 as a fluorinating agent. This method has great potential for making important aromatic fluorine compounds.

The same NF_4BF_4 fluorination technique was applied to highly fluorinated benzenes and was found to give controlled addition of fluorine to the ring, thereby generating 1,4-cyclohexadienes and cyclohexenes.

PERSONNEL

Dr. C. J. Schack has been the principal investigator on this program. Valuable consultation on spectroscopic matters has been furnished by Dr. K. O. christe. Both Drs. Christe and L. R. Grant have provided helpful discussion.

INTERACTIONS

PAPERS

An invited paper entitled "Reactions of Chlorine Fluorosulfate with Fluorocarbons," was presented at the 175th ACS National Meeting in Anaheim, California in March 1978. This paper was part of the Symposium on Positive Halogen Chemistry honoring Dr. J. M. Shreeve, the recipient of the Fluorine Division Award for Creative Work in Fluorine Chemistry.

A paper entitled " $\text{SF}_5\text{O}-$ and $\text{CF}_3\text{O}-$ Containing Fluorocarbons," was presented at the Fourth Winter Fluorine Symposium sponsored by the Fluorine Division of the American Chemical Society at Daytona Beach, Florida in January 1979.

A paper entitled "Fluorine Perchlorate Reactions with Fluorocarbons" was presented at the American Chemical Society/Chemical Society of Japan Chemical Congress at Honolulu, Hawaii in April 1979.

A paper entitled "Iodine Fluorosulfate Reactions with Fluorocarbons" has been accepted for presentation at the Fall 1980 ACS National Meeting in San Francisco. In addition, Dr. Schack has been invited to chair a session at that meeting.

All of these papers were coauthored with K. O. Christe.

CONSULTATION

Advice, consultation and material (several pounds) was provided to the Science Center of Rockwell International regarding the properties and handling characteristics of chlorine fluorosulfate. This was in support of their work on Air Force Contracts No. F29601-78-C-0023 and No. F29601-76-C-0070, Kirtland AFB, which were concerned with the use of ClSO_2F in

the generation of singlet delta oxygen for application in a potential iodine chemical laser system.

Experimental tests were conducted on the scavenging of CF_4 by liquid sodium in support of an Air Force krypton fluoride chemical laser study. Consultation and multigram quantities of the salt $\text{O}_2^+\text{AsF}_6^-$ were supplied to the Science Center of Rockwell International in support of their Air Force contract (No. F29601-78-C-0039) concerned with chemiluminescence of thermally generated O_2F .

A batch of a novel azido, nitramine compound was synthesized for another group at Rocketdyne for testing as a plasticizer on an Air Force program, Contract No. F08635-79-C-0291, concerned with reduced flame temperature propellants. In addition, the synthesis and analysis of two proprietary energetic materials was carried out on company funds. These materials, which are currently under test at Rocketdyne and the Science Center of Rockwell International, have potential in high energy laser systems of interest to the Air Force and Army.

PATENTS

Assistance was provided to the Air Force Patent Office, Boston, in updating and completing patent applications disclosed under this program. These patents are expected to issue in the near future and are entitled:

1. "The Preparation of Fluorocarbon Halides Using Halogen Fluoro-sulfates," C. J. Schack and K. O. Christe.
2. "The Synthesis of Fluorocarbon Esters," C. J. Schack and K. O. Christe.

In addition, another patent disclosure was filed as a result of work on this program and the application is being prepared for submission to the Patent Office. This application is entitled:

3. "Introduction of Fluorine Into An Aromatic Ring," K. O. Christe and C. J. Schack.

Recently, another disclosure was filed on the ISO_3F -Olefin reactions and is entitled:

4. "Fluorocarbon Fluorosulfate Iodides," by C. J. Schack.

PUBLICATIONS

1. "Reactions of Electropositive Chlorine Compounds with Fluorocarbons," by C. J. Schack and K. O. Christe, Israel J. Chem., 17, 20 (1978).
2. "Improved Syntheses of Some Sulfur Fluoride and Oxyfluoride Peroxides," by C. J. Schack and K. O. Christe, Inorg. and Nuclear Chem. Letters, 14, 293 (1978).
3. "Fluoroacyl Hypochlorites and Ester Derivatives," by C. J. Schack and K. O. Christe, J. Fluorine Chem., 19, 325 (1978).
4. "Introduction of Functional Groups into Some Chlorofluorocarbon Ethers," by C. J. Schack and K. O. Christe, J. Fluorine Chem., 14, 519 (1979).
5. "Halogen Fluorosulfate Reactions with Fluorocarbons," by C. J. Schack and K. O. Christe, J. Fluorine Chem., to appear July 1980.
6. "Iodine Fluorosulfate Reactions with Fluorocarbons," by C. J. Schack and K. O. Christe, to be submitted for publication.
7. "Substitution and Addition Reactions of NF_4BF_4 with Fluorocarbons," by C. J. Schack and K. O. Christe, to be submitted for publication.

APPENDIX A

IMPROVED SYNTHESSES OF SOME SULFUR FLUORIDE AND OXYFLUORIDE PEROXIDES

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IMPROVED SYNTHESSES OF SOME SULFUR FLUORIDE AND OXYFLUORIDE PEROXIDES

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INTRODUCTION

The sulfur fluoride peroxides, SF_5OOSF_5 and SF_5OOSF_5 , are potentially very useful sources for introducing the SF_5 -group into other substrates. Their utility in this regard has not been widely explored. This is attributable in part to the relatively poor yields reported (1) for the various synthetic procedures. Improvements in these methods were sought and the results are described in this paper together with a simplified photolytic process for the synthesis of $\text{FO}_2\text{SOOSF}_5(\text{S}_2\text{O}_6\text{F}_2)$.

EXPERIMENTAL

Materials and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps, 316 stainless steel bellows-seal valves and a Heise Bourdon tube-type pressure gauge. Metal fluorides, CsF and KF, were fused in a platinum crucible, then cooled and powdered in a drybox prior to use. Thionyl tetrafluoride was prepared from SOF_2 and F_2 according to Ruff and Lustig (2) and SF_5OCl (3), CsSF_5O (4), and ClSO_3F (5) were synthesized by literature methods.

SF_5OOSF_5 . In a typical experiment, a prepassivated 30-ml stainless steel cylinder was loaded with dry, powdered CsF (19.6 mmol). After cooling to -196° , SOF_4 (6.36 mmol) and $\text{S}_2\text{O}_6\text{F}_2$ (4.55 mmol) were condensed into the cylinder. After warming to ambient temperature the cylinder was placed for 2 1/2 days in an oven maintained at 35° . Work-up of the reaction mixture was accomplished by vacuum fraction of the volatile products through a series of U traps cooled to -78° , -78° , and -196° . By-product oxygen, a few cm^3 , was pumped away. The -196° trap contained 2.39 mmol of a mixture of SOF_4 and the by-product SO_2F_2 while the -78° traps contained the desired product SF_5OOSF_5 (3.67 mmol), 81% yield, based on $\text{S}_2\text{O}_6\text{F}_2$ which was identified by its vapor pressure, infrared and ^{19}F nmr spectra (6,7). The weight gain of the solid (537 mg) corresponded reasonably well with that calculated (512 mg) for the formation of 4.55 mmol of CsSO_3F and 1.19 mmol of CsSF_5O . The latter number was calculated from the amount of SF_4O not recovered in the form of a volatile product.

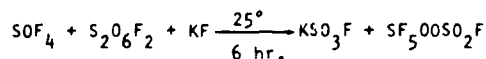
SF_5OOSF_5 . A 300 ml Pyrex bulb equipped with a Fischer-Porter Teflon stopcock and cooled to -196° was loaded with SF_5OCl (10.8 mmol). While allowing to warm to ambient temperature, the bulb was irradiated for 1 hr. using a Hanovia 100-W utility lamp (Catalog No. 30620). The products

were separated by fractionation through U traps cooled to -78 , -95 , and -196° . The warmer traps contained SF_5OOSF_5 (4.60 mmol, 85% yield) which was identified by its vapor pressure (8) and infrared and mass spectroscopy (3). By-product Cl_2 , and the decomposition products, SOF_4 and SiF_4 were found in the -196° trap.

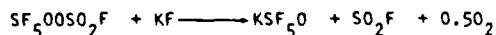
$\text{S}_2\text{O}_6\text{F}_2$. Chlorine fluorosulfate (18.8 mmol) was charged into a 500 ml Pyrex bulb cooled to -196° . After removing the -196° bath, the bulb and contents were irradiated with the Hanovia lamp for 4 hr. The products were separated by fractional condensation through traps cooled to -30 , -78 , and -196° . Only a trace of low volatility, orange liquid presumably $\text{ClO}_2\text{SO}_3\text{F}$, was retained at -30° . The -196° fraction consisted of 9.69 mmol of material which was identified as Cl_2 with traces of SiF_4 and ClSO_2F . In the trap cooled to -78° , pure, colorless $\text{S}_2\text{O}_6\text{F}_2$ (8.79 mmol, 94% yield) was obtained.

DISCUSSION

Two syntheses of $\text{SF}_5\text{OOS}_2\text{F}$ have previously been reported. In the first, when equimolar quantities of SF_5OOSF_5 and $\text{S}_2\text{O}_6\text{F}_2$ were photolyzed, equal amounts of $\text{SF}_5\text{OOS}_2\text{F}$ and of the starting materials were found (6). Since the desired $\text{SF}_5\text{OOS}_2\text{F}$ cannot be physically separated from $\text{S}_2\text{O}_6\text{F}_2$, the latter had to be destroyed by reaction with I_2 . Because this synthesis is based on an equilibrium and the unreacted $\text{S}_2\text{O}_6\text{F}_2$ must be removed chemically, the yield of this process is inherently low. The second reported method (9), involved oxidation of SOF_4 with $\text{S}_2\text{O}_6\text{F}_2$ in the presence of KF .

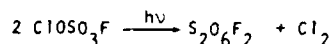


Moderate yields were obtained (to 60%) due to the following side reaction.



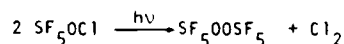
With CsF this side reaction was reportedly so fast as to preclude isolation of any $\text{SF}_5\text{OOS}_2\text{F}$. On attempting to repeat this reaction we found that very little $\text{SF}_5\text{OOS}_2\text{F}$ was formed with KF but that with CsF at ambient temperature a high yield (up to 91%) of $\text{SF}_5\text{OOS}_2\text{F}$ was realized. Contact times of several days were required to achieve a complete conversion of the limiting reagent, $\text{S}_2\text{O}_6\text{F}_2$. Attempts to increase the rate of formation revealed that the reaction is very temperature dependent. Thus, after 3 days at 50° only decomposition products were found, and after a similar period at 40° , the observed yield was only 34%. Reproducible, relatively high yields of 75-85% were obtained by heating the reaction mixture at 35° in an oven for 2-3 days. Comparable yields were possible with 1 day reaction times if CsSF_5O was employed instead of CsF and SOF_4 . Thus, the procedure involving moderate heating of CsF , SOF_4 , and $\text{S}_2\text{O}_6\text{F}_2$ in a static system appears to be the preferred synthesis for $\text{SF}_5\text{OOS}_2\text{F}$. The $\text{S}_2\text{O}_6\text{F}_2$ starting material is readily prepared from F_2 and SO_3 in small quantities in a static reactor (9) and in larger quantities in a flow reactor using AgF_2 as a catalyst (10). Two drawbacks to this reaction are, (I) elemental fluorine is required which many laboratories are not equipped to handle and (II) the explosive by-product SO_3F_2 is produced

which must be disposed of and not collected (11). A simple alternative synthesis involves the photolysis of chlorine fluorosulfate (5).



Whereas previously this reaction was carried out at -78° for several hours, it has now been determined that an ambient temperature photolysis for 2-4 hr gives $\text{S}_2\text{O}_6\text{F}_2$ in 94-97% yield. Thus, a practical alternate route is available to this peroxide.

Numerous methods have been described (1) for the preparation of SF_5OOSF_5 , but most of them suffer from low yields (2-20%). The highest yield reported (12) was achieved in a photolytic reaction of SF_5Cl and O_2 which entailed circulation of the materials and continuous removal of SF_5OOSF_5 to preclude its decomposition. Previously we had noted (3) that SF_5OCl , when subjected to UV-photolysis for several hours in Pyrex vessels, gave good yields (65%) of SF_5OOSF_5 .



It has now been found that shortening the photolysis period to 1 hr from the time warming begins increases the yields of peroxide to 8%. This is comparable to the best results achieved by any other method. In addition, the shorter irradiation time reduced the amount of the inseparable by-product SF_5OSF_5 to less than 1% compared to the 3% previously observed for this reaction (3), or the higher percentage observed for most other systems. Beginning the photolysis immediately on warming above -196° , limits loss of SF_5OCl through decomposition to SOF_4 and ClF .

In general then, it has been shown that simple, direct synthetic procedures are available for the preparation of these sulfur fluoride or oxyfluoride peroxides in high yield. Furthermore, these methods minimize by-product formation and involve by-products which are easily separable from the desired product. These improved synthetic methods increase the accessibility of these compounds and should enhance their utilization.

ACKNOWLEDGEMENT

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APPENDIX B

FLUOROACYL HYPOCHLORITES AND ESTER DERIVATIVES

Journal of Fluorine Chemistry, 12 (1978) 325-330
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 Received May 19, 1978

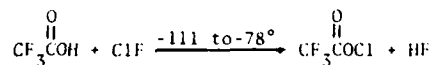
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SHORT COMMUNICATION

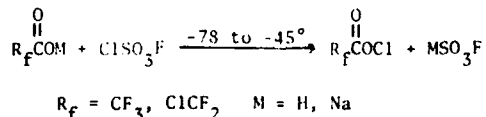
Fluoroacyl Hypochlorites and Ester Derivatives

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 Canoga Park, California 91304

Recently Des Marteau [1] reported the preparation and isolation of $\text{CF}_3\text{CO}_2\text{Cl}$ (and $\text{CF}_3\text{SO}_3\text{Cl}$) by the low temperature reaction of the corresponding acids with ClF .



In this paper we would like to report the results of an independent simultaneous study. In our study, the chlorinating agent employed was chlorine fluorosulfate [2] and either the acid or its alkali metal salt were used as substrates.



For cases where a volatile acyl hypochlorite is formed, the use of ClSO_3F instead of ClF allows easier product separation because the by-product HSO_3F is much less volatile than HF . When salts are employed, essentially no separation problems are encountered since the by-products are solids. Although the reaction of ClF and acid salts was not tested, based on our experience [3] ClSO_3F is superior to ClF in chlorinating anionic species. In our preparations using ClSO_3F somewhat higher reaction temperatures were employed than those reported for ClF [1]. Complete reaction of the ClSO_3F occurred. The product acyl hypochlorite was essentially the only volatile product formed and it was purified by fractional condensation in a vacuum line with about 10% material loss due to decomposition during handling.

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B-1

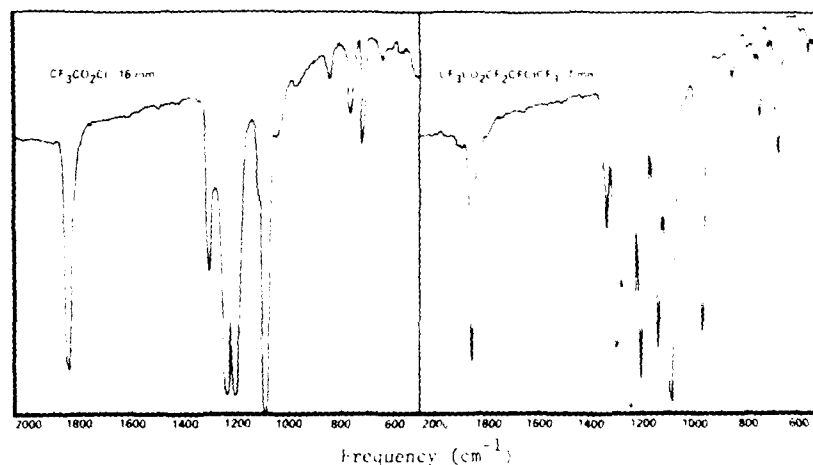
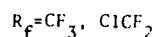
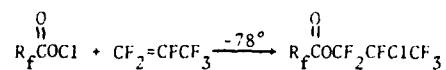


Figure 1. Gas Phase Infrared Spectra

The properties observed for $\text{CF}_3\text{CO}_2\text{Cl}$ agree well with those given by Des Marteau [1]. In addition, it was found that adequate passivation of container surfaces and pretreatment with the compound itself permitted reproducible gas phase infrared spectra to be obtained. The spectrum is shown in Fig. 1 and the observed bands are consistent with an acyl hypochlorite structure. Comparison with related species allows assignment of particular bands. Thus, the band at 1844 cm^{-1} is clearly the C=O stretch which occurs at 1852 cm^{-1} in $\text{CF}_3\text{CO}_2\text{CF}_3$ [4]. The three bands at 1308, 1241, and 1206 cm^{-1} are C-F stretching modes typically noted for CF_3 compounds as strong bands in this area [5,6]. The intense band at 1093 cm^{-1} is the C-O stretch which occurs in the range of $1109\text{--}1120\text{ cm}^{-1}$ in a series of $\text{R}_f\text{CO}_2\text{R}_f$ esters [7] while the weak band at 844 cm^{-1} is the C-C stretching vibration which is normally weak and occurs in the $800\text{--}900\text{ cm}^{-1}$ region in similar compounds [5,6]. Of the remaining two bands, the one at 719 cm^{-1} can be assigned to the Cl-O stretching mode based on Des Marteau's observation of an intense polarized Raman band at 716 cm^{-1} and by comparison with other hypochlorites [8]. Finally, then, the medium weak 765 cm^{-1} absorption is ascribed to the CF_3 deformation mode which is in agreement with the $693\text{--}781\text{ cm}^{-1}$ range reported [5,6] for similar compounds.

A reaction typical of positively polarized chlorine species [9] is their addition across C=C bonds. Such derivative forming reactions are useful for the characterization of these species and in the present case also serve as a very convenient synthetic method for fluorocarbon esters.



The infrared spectrum of a typical ester is shown in Fig. 1 and its ^{19}F nmr spectrum is given in Fig. 2. Although two isomeric addition products

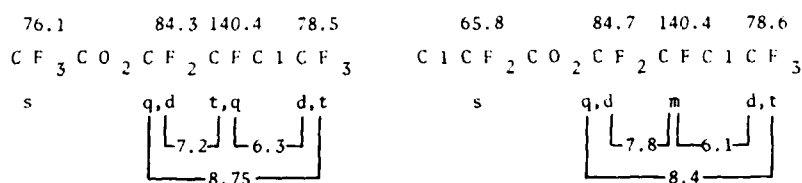
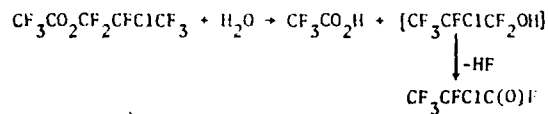


Figure 2. ^{19}F Chemical Shift in ppm Upfield Relative to CFCl_3 Internal Reference; S, singlet; d, doublet; t, triplet; q, quartet; m, multiplet

are theoretically possible, only the one expected for a directed, polar addition was found in each reaction. Controlled hydrolysis of $\text{CF}_3\text{CO}_2\text{CF}_2\text{CFCF}_3$ in CFCF_3 solution proceeds according to:



Although hydrolytically unstable, these esters are stable at ambient temperature and can be stored in glass.

EXPERIMENTAL

Caution: Fluoroacyl hypochlorites are explosives, possibly even in the gas phase, and should be handled with appropriate safety precautions.

Volatile materials were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps, 316 stainless steel bellows seal valves and a Heise Bourdon tube-type pressure gauge. Transfers outside the vacuum line were carried out in a drybox. Infrared spectra were obtained using 5 cm path stainless steel cells with AgCl windows and a PE Model 283 spectrophotometer. Mass spectra were measured with an EA1 Quad 300 quadrupole spectrometer and ^{19}F nmr spectra were determined with a Varian EM390 spectrometer operating at 84.6 MHz. Fluorocarbon starting materials were purchased from PCR Inc. and ClSO_3F was prepared as reported [2].

$\text{CF}_3\text{CO}_2\text{Cl}$. A 30 ml stainless steel cylinder containing $\text{CF}_3\text{CO}_2\text{Na}$ (5.24 mmol) was cooled to -196° and loaded with freshly purified ClSO_3F (2.93 mmol). The reaction cylinder was then maintained at -45° for 16 hr. The volatile products were separated by fractional condensation through a series of U traps cooled to -78° , -112° , and -196° . All material passed the -78° trap while the -196° trap contained 0.6 mmol of a mixture of CF_3Cl , CO_2 , COF_2 and Cl_2 . The material retained at -112° was a very pale yellow liquid. Removal of part of this material to another trap followed by careful warming resulted in decomposition to an equimolar mixture of CF_3Cl and CO_2 . The observed weight change (38 mg) of the solids in the cylinder agreed well with that calculated (41 mg) for the conversion of 2.93 mmol $\text{CF}_3\text{CO}_2\text{Na}$ to NaSO_3F . On one occasion, a sample of $\text{CF}_3\text{CO}_2\text{Cl}$, when allowed to warm to a temperature resulting in 40 mm vapor pressure, exploded in the vacuum line forming mainly CF_3Cl and CO_2 but also some COF_2 , CF_4 , C_2F_6 , and Cl_2 . In carefully passivated IR cells which were pretreated with some $\text{CF}_3\text{CO}_2\text{Cl}$, a reproducible infrared spectrum of this acyl hypochlorite was obtained, cm^{-1} : 1844(S), 1308(M), 1241(S), 1206(S), 1093(S), 844(W), 765(W) and 719(MW).

Fig. 1. Decomposition rates varied considerably from minutes to hours depending on the sample. The primary decomposition product in the cells was $\text{CF}_3\text{CO}_2\text{H}$ indicating incomplete passivation despite the precautions taken.

$\text{ClCF}_2\text{CO}_2\text{Cl}$. Chlorodifluoroacetic acid (2.80 mmol) was placed in a 30 ml stainless steel cylinder. After cooling to -196° and evacuating, ClSO_3F (2.91 mmol) was condensed in and the reaction allowed to proceed at -45°

for two days. Separation of the products was effected by keeping the cylinder at -30° (to retain HSO_3F) and pumping the volatile materials through U traps cooled to -78 and -196° . The latter contained 0.24 mmol of Cl_2 and SO_2F_2 , while the former contained the pale yellow liquid $\text{ClCF}_2\text{CO}_2\text{Cl}$. A sample of $\text{ClCF}_2\text{CO}_2\text{Cl}$, allowed to stand at ambient temperature in the vacuum line for two hours, was found to have completely decomposed to an equimolar mixture of CF_2Cl_2 and CO_2 . On one occasion a sample of $\text{ClCF}_2\text{CO}_2\text{Cl}$ warmed to about 0° exploded when a valve was opened rapidly to allow it to expand. This contained explosion produced primarily CF_2Cl_2 and CO_2 , but also some COF_2 and Cl_2 .

$\text{CF}_3\text{CO}_2\text{CF}_2\text{CFCFClCF}_3$. To a 2.03 mmol sample of $\text{CF}_3\text{CO}_2\text{Cl}$ contained in a U-trap at -78° , hexafluoropropylene (2.72 mmol) was slowly added. After several hours the mixture was warmed to ambient temperature for 1 hour prior to fractional condensation through traps cooled to -78 and -196° . The -196° fraction consisted of one mmol C_3F_6 and 0.27 mmol each of CF_3Cl and CO_2 . The material retained at -78° was a colorless liquid and was identified as $\text{CF}_3\text{CO}_2\text{CF}_2\text{CFCFClCF}_3$ (1.70 mmol, 84% yield) on the basis of its vapor density molecular weight (297 found vs. 298.5 g/mol calculated), and controlled hydrolysis to a 1:1 mixture of $\text{CF}_3\text{CFCFClCF}_3$ [10] and $\text{CF}_3\text{CO}_2\text{H}$. Its spectroscopic properties confirmed this identification: infrared, cm^{-1} ; 1856 (S), 1335 (M), 1297 (S), 1249 (VS), 1205 (S), 1137 (S), 1088 (VS), 970 (S), 850 (W), 740 (W), 671 (MW); mass spectrum, 40 eV; m/e (assign., rel. intens.) 298 (M, 0.01), 279 (M-F, 0.03), 263 (M-Cl, 0.03), 244 (M-F, Cl, 0.05), 229 (M- CF_3 , 0.14), 185 ($\text{C}_3\text{F}_6\text{Cl}$, 4.7), 166 ($\text{C}_3\text{F}_6\text{O}$; 0.04), 163 ($\text{C}_3\text{F}_5\text{O}_2$, 0.06), 135 ($\text{C}_2\text{F}_5\text{O}$, $\text{C}_2\text{F}_4\text{Cl}$, 6.8), 131 (C_3F_5 , 1.0), 119 (C_2F_5 , 0.3), 116 ($\text{C}_2\text{F}_3\text{Cl}$, 1.8), 113 ($\text{C}_2\text{F}_3\text{O}_2$, 0.6), 109 ($\text{C}_3\text{F}_3\text{O}$, 0.1), 100 (C_2F_4 , 3.3), 97 ($\text{C}_2\text{F}_3\text{O}$, 30), 94 ($\text{C}_2\text{F}_2\text{O}_2$, 0.7), 85 (CF_2Cl , 17), 81 (C_2F_3 , 0.5), 78 ($\text{C}_2\text{F}_2\text{O}$, 0.9), 69 (CF_3 , 100), 66 (COF_2 , 1.7), 51 (CFCFCl , 0.6), 50 (CF_2 , 3.6), 47 (COF , 3.5), 44 (CO_2 , 3.6); ^{19}F nmr; Fig. 2.

$\text{ClCF}_2\text{CO}_2\text{CF}_2\text{CFCFClCF}_3$. Using the above described conditions, $\text{ClCF}_2\text{CO}_2\text{Cl}$ (2.30 mmol) was reacted with C_3F_6 (2.46 mmol) to furnish 0.60 mmol each of CF_2Cl_2 and CO_2 together with 0.76 mmol of unreacted C_3F_6 . The colorless liquid $\text{ClCF}_2\text{CO}_2\text{CF}_2\text{CFCFClCF}_3$ (1.70 mmol, 74% yield) was identified spectroscopically: infrared, cm^{-1} ; 1856 (S), 1300 (MS), 1270 (MS), 1238 (VS), 1193 (S), 1135 (S), 1096 (VS), 985, 975 (S, doublet), 848 (W), 736 (W), 690 (W, br), 617 (W); mass spectrum, 40 eV; m/e (assign., rel. intens.) 314 (M, 0.05), 295 (M-F, 0.03), 279 (M-Cl, 0.02), 245 (M- CF_3 , 0.02),

229 (M-CF₂Cl, 0.15), 185 (C₃F₆Cl, 31), 166 (C₃F₆O, 0.41), 150 (C₃F₆, 3.1),
 147 (C₃F₅O, 0.5), 135 (C₃F₄Cl, 12), 131 (C₃F₅, 2.4), 116 (C₂F₃Cl, 5.8),
 113 (C₂F₃O₂, 2.9), 100 (C₂F₄, 7), 97 (C₂F₃O, 22), 94 (C₂F₂O, 5.5),
 85 (CF₂Cl, 100), 78 (C₂F₂O, 6), 69 (CF₃, 55), 66 (CFCl, 6), 50 (Cl₂, 12),
 47 (COF, 10), 44 (CO₂, 24): ¹⁹F nmr; Fig. 2.

ACKNOWLEDGEMENT

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APPENDIX C

INTRODUCTION OF FUNCTIONAL GROUPS INTO SOME CHLOROFLUOROCARBON ETHERS

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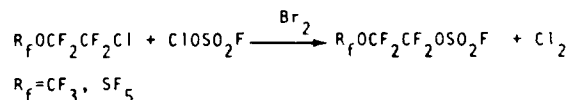
SHORT COMMUNICATION

Introduction of Functional Groups into Some Chlorofluorocarbon Ethers

CARL J. SCHACK and KARL O. CHRISTE

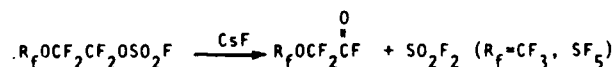
Rocketdyne, a Division of Rockwell International
 Canoga Park, California 91304, U.S.A.

The addition of hypochlorites, such as CF_3OCl and SF_5OCl , to perfluoroolefins is a straightforward route to chlorofluorocarbon ethers [1,2]. These materials are very stable entities. Both the hypochlorite addition and the derived ethers would be more useful if functional groups could be introduced into these compounds. This paper describes a method to achieve this goal. It involves the conversion of the $-\text{CF}_2\text{Cl}$ end group into a $-\text{CF}_2\text{OSO}_2\text{F}$ group:



This reaction was found to occur in high yield (70-90%) but at a slow rate. Two to three weeks were required for complete conversion of the starting material at 110-140°. The addition of 10-20 mole % of bromine which results in *in situ* BrOSO_2F formation was necessary to obtain these reaction rates. Pure ClOSO_2F or $\text{F}_2\text{SO}_2\text{SO}_2\text{F}$ did not produce appreciable reaction under the same conditions. Higher temperatures were not investigated since attack on the stainless steel reactors by the halogen fluorosulfates becomes significant. In view of the general inertness of the $-\text{CF}_2\text{Cl}$ group, it is encouraging that high conversions are obtainable and that the ether function is unaffected.

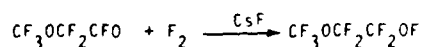
The resulting fluorocarbon fluorosulfates can be converted into the corresponding acyl fluorides in essentially quantitative yield via the CsF catalyzed elimination of sulfuryl fluoride [3].



Both of these acyl fluorides have been reported as products from other reactions. Thus, $\text{CF}_3\text{OCF}_2\text{CFO}$ was obtained in 3% yield from the thermal, flow tube reaction of perfluoropropene and oxygen [4] and also from $\text{CF}_3\text{OCF}_2\text{CO}_2\text{K}$ (unspecified origin) [5] in 52% yield. Additional

characterizing data for these compounds has been obtained (see Experimental Section). The sulfur analogue was reported to result, unexpectedly and inexplicably, from the reaction of ozone and $\text{SF}_5\text{CF}=\text{CF}_2$ with an estimated yield of 67%. Our observed properties are in good agreement with those previously reported [6].

It has previously been shown for $\text{SF}_5\text{OCF}_2\text{CFO}$ that these acid fluorides can readily be converted to typical derivatives, such as acid and amide [6]. We have found that another derivative, the hypofluorite, can readily be made in high yield.



This reactive compound is easily identified by its ^{19}F NMR chemical shift, characteristic for the hypofluorite fluorine [7] as are the SF_5^- , $-\text{SO}_3\text{F}$, and $-\text{CFO}$ groups which are summarized in Table I.

Table I: ^{19}F NMR Data Chemical Shifts (ppm)^a and Coupling Constants (Hz)

Compound	$\text{RF}_n\text{O}-$	$-\text{CF}_2-$	$-\text{CF}_2-$	$-\text{F}$
$\text{CF}_3\text{OCF}_2\text{CF}_2\text{OSO}_2\text{F}$	57.6(t) (J=8.6)	92.1(q) (J=8.6)	90.0(d) (J=8.2)	-49.6(t) (J=8.3)
$\text{CF}_3\text{OCF}_2\text{CFO}$	56.3(t) (J=8.5)	79.6(q,d)		-13.4(t) (J=2.8)
$\text{CF}_3\text{OCF}_2\text{CF}_2\text{OF}$	56.0(t) (J=8.5)	85.8(q) ^b (J=8.5)	98.1(d) (J=8.5)	-138.8(q) (J=8.5)
$\text{SF}_5\text{OCF}_2\text{CF}_2\text{OSO}_2\text{F}$	-60.2(ax.) -72.5(eq.)	89.1(q) (J=11.6)	88.4(d) (J=7.9)	-49.7(t) (J=7.9)
$\text{SF}_5\text{OCF}_2\text{CFO}$	-61.4(ax.) -72.0(eq.)	77.9(q,d) (J=10.7, 3.4)		-13.2(t) (J=3.4)

a) Upfield from internal CFCl_3 . b) Apparent quintet due to approximately equal coupling to $\text{CF}_3\text{O}-$ and OF Fluorines

In summary, the above results demonstrate that the successful conversion of the $-\text{CF}_2\text{Cl}$ group to a fluorosulfate offers a simple and efficient route to a variety of conventional functional groups.

EXPERIMENTAL

The apparatus and instruments used in this work have previously been described [8]. Literature procedures were employed to prepare $\text{CF}_3\text{OCF}_2\text{CF}_2\text{Cl}$ [1,2], $\text{SF}_5\text{OCF}_2\text{CF}_2\text{Cl}$ [1,2], ClOSO_2F [9], and $\text{S}_2\text{O}_6\text{F}_2$ [10]. $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OSO}_2\text{F}$. A 30 ml stainless steel cylinder was loaded with $\text{CF}_3\text{OCF}_2\text{CF}_2\text{Cl}$ (1.38 mmol), ClOSO_2F (2.10 mmol), and Br_2 (0.2 mmol) at

-196°: After warming to ambient temperature the reactor was heated for two weeks at 110°. Fractional condensation through U-traps cooled to -45, -78, -112, and -196° was used to separate the $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OSO}_2\text{F}$ product from the by-products BrOSO_2F , $\text{S}_2\text{O}_5\text{F}_2$, BrCl and small amounts of unreacted $\text{CF}_3\text{OCF}_2\text{CF}_2\text{Cl}$ and ClOSO_2F . The desired $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OSO}_2\text{F}$ was retained in both the -78 and -112° traps and was treated with KI to remove traces of colored impurities furnishing the purified material in 90% yield. The product was identified by infrared, cm^{-1} : 1498(s), 1295(s), 1252(s), 1173(s), 1157(s), 1143(s), 1091(s), 928(w), 915(w), 840(m), 769(w), 682(v-w), 551(w); mass spectrum, 40 ev, M/e (assign. rel. intens.) 265 (M-F, 0.02), 252 (M-O₂, 0.02), 249 (M-O, F, 0.02), 199 (M-CF₃O, 0.9), 185 (M-SO₃F, 0.8), 182 (C₃F₅O₂, 0.35), 163 (C₃F₅O₂, 0.06), 149 (CF₂SO₃F, 3.7), 135 (C₂F₅O, 4), 119 (C₂F₅, 45), 102 (SO₂F₂, 0.35), 100 (C₂F₄, 0.7), 97 (C₂F₃O, 4.5), 83 (SO₂F, 53), 80 (SO₃, 6), 69 (CF₃, 100), 67 (SO₂F, 8), 64 (SO₂, 5), 50 (CF₂, 3.5), 48 (SO, 4), and 47 (COF, 16): ¹⁹F NMR.

$\text{SF}_5\text{OCF}_2\text{CF}_2\text{OSO}_2\text{F}$. By analogy with $\text{CF}_3\text{OCF}_2\text{CF}_2\text{Cl}$, a sample of $\text{SF}_5\text{OCF}_2\text{CF}_2\text{Cl}$ (1.20 mmol) was reacted with ClOSO_2F (2.26 mmol) and Br_2 (0.5 mmol) for three weeks at 130°. The desired product was retained in the -78° trap and was obtained in 71% yield after purification. Identification was based on infrared, cm^{-1} : 1495(s), 1265(s), 1230(s), 1203(s), 1160(s), 1087(s), 947(s), 930(s), 870(s), 845(s), 822(s), 766(m), 600(s), 557(m); mass spectrum, 40 ev, M/e (assign. rel. intens.) 323 (M-F, vw), 310 (M-O₂, vw), 243 (SF₅OC₂F₄, 0.03), 199 (C₂F₄SO₃F, 2.4), 193 (SF₅OCF₂, 0.2), 149 (CF₂SO₃F, 2.7), 127 (SF₅, 100), 119 (C₂F₅, 46), 108 (SF₄, 0.9), 105 (SF₃O, 55), 100 (C₂F₄, 1.3), 97 (C₂F₃O, 3), 89 (SF₃, 11.5), 83 (SO₂F, 60), 70 (SF₂, 2.8), 69 (CF₃, 16), 67 (SF₅O, 11), 66 (CF₂O, 2), 64 (SO₂, 6.5), 51 (SF, 1), 50 (CF₂, 8), 48 (SO, 8), and 47 (CFO, 25): ¹⁹F NMR.

$\text{CF}_3\text{OCF}_2\text{CFO}$ and $\text{SF}_5\text{OCF}_2\text{CFO}$. Both compounds were prepared in 95 + % yield by heating a sample (0.5 mmol) of the respective fluorosulfate in the presence of 10 mmol CsF, for 14 hrs to 110°. The only volatile product was SO_2F_2 . The acyl fluorides were obtained by vacuum pyrolysis of the formed salt, $\text{R}_f\text{OCF}_2\text{CF}_2\text{OCs}$. For $\text{CF}_3\text{OCF}_2\text{CFO}$, the vapor density was 179 g/mol (theory=182). The infrared spectrum observed was, cm^{-1} : 1893(s), 1340(m), 1280(s), 1247(vs), 1198(m), 1145(vs), 1092(m), 925(w), 910(w), 831(vw), 760(vw), 732(vw), 700(vw) and the mass spectrum, 40 ev, M/e (assign. rel. intens.), 135(M-CFO, 5), 97(M-CF₃O, 10), 85(CF₃O, 8), 78(C₂F₂O, 0.5), 69(CF₃, 100), 66(CF₂O, 1.5), 50(CF₂, 12), and 47(CFO).

28). The ^{19}F NMR spectrum agreed with the literature [4]. For $\text{SF}_5\text{OCF}_2\text{CFO}$ the observed vapor density was 342 g/mol (theory=344). The observed infrared spectrum was as reported [6] and in addition showed a strong 603 cm^{-1} band which was beyond the range of the previous study. The mass spectrum noted was; 193(M-CFO, 1.6), 127(SF_5 , 100), 108(SF_4 , 2), 105(SF_3O , 26), 97(M- SF_5O , 12), 89(SF_{31} , 15), 86(SF_2O , 1), 83(SO_2F , 0.5), 69(CF_3 , 28), 67(SFO , 2.6), 66(CF_2O , 1.2), 50(CF_2 , 4.5), and 47(CFO , 23). The ^{19}F NMR was as reported [6].

$\text{CF}_3\text{OCF}_2\text{CF}_2\text{OF}$. A sample of $\text{CF}_3\text{OCF}_2\text{CFO}$ (0.27 mmol) was allowed to react with F_2 (2.2 mmol) in the presence of CsF (~ 8 mmol) by slowly warming the condensed reactants to ambient temperature overnight. After removal of the excess F_2 by pumping at -196° , the only volatile product found was $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OF}$ in 88% yield. In addition to the ^{19}F NMR spectrum further identification of this hypofluorite was obtained from its infrared spectrum, cm^{-1} ; 1347(M), 1291(S), 1249(VS), 1214(S), 1194(S), 1156(VS), 1086(M), 895(MW), 804(W), 697(W). Below M/e 100 the mass spectrum was qualitatively much like $\text{CF}_3\text{OCF}_2\text{CFO}$ but showed weak peaks at 201(M-F), 185(M-OF) and intense 135($\text{C}_2\text{F}_5\text{O}$), 119(C_2F_5), and 116($\text{C}_2\text{F}_4\text{O}$) peaks.

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APPENDIX D

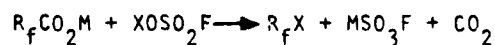
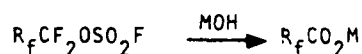
HALOGEN FLUOROSULFATE REACTIONS WITH FLUOROCARBONS

HALOGEN FLUOROSULFATE REACTIONS WITH FLUOROCARBONS

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ABSTRACT

The scope of the reaction of simple fluorocarbon halides with chlorine fluorosulfate and mixtures of chlorine and bromine fluorosulfate to produce $R_f\text{OSO}_2\text{F}$ compounds has been investigated. It is shown that in many cases even primary chlorine in $-\text{CF}_2\text{Cl}$ groups can be replaced by $-\text{OSO}_2\text{F}$. Primary bromine or iodine in $-\text{CF}_2\text{X}$ are more readily replaced. The mechanism of this replacement reaction has been established by the isolation of the metastable iodine III intermediate $R_f\text{I}(\text{OSO}_2\text{F})_2$. Neither secondary chlorine nor bromine in $-\text{CFX}-$ groups is affected. With the secondary iodide, $i\text{-C}_3\text{F}_7\text{I}$, the salt $[(i\text{-C}_3\text{F}_7)_2\text{I}]^+ [\text{I}(\text{OSO}_2\text{F})_4]^-$ is formed. Furthermore, it has been found that ClOSO_2F is capable of converting fluorocarbon acids or their derivatives into fluorocarbon halides. A combination of these two ClOSO_2F reactions with the known conversion of $R_f\text{CF}_2\text{OSO}_2\text{F}$ to the corresponding fluorocarbon acid offers a novel, high yield chain shortening reaction for the otherwise unreactive fluorocarbon halides according to:



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D-1

INTRODUCTION

Shortly after the discovery by Cady and coworkers [1-4] of the halogen fluorosulfates and peroxydisulfuryl difluoride, their reactivity with select fluorocarbon compounds was noted. This activity included addition to olefins [3,4], displacement of chlorine, bromine, or iodine from methyl compounds [5,6] and a few others [7] to give ROSO_2F (commonly written RSO_2F), as well as cleavage of anhydrides [8]. Iodofluorocarbons were also converted successfully to fluorocarbon fluorosulfates by treatment with fluorosulfonic acid at elevated temperature [9]. However, the scope of these reactions, particularly the displacement of halogen by fluorosulfate was not defined. Since many fluorocarbon halides would be more useful if the halide could be replaced by a more reactive group such as the fluorosulfate, it was the goal of this work to determine the practical extent of this displacement reaction. In addition, the utility of chlorine fluorosulfate in decarboxylating fluorocarbon acids was discovered. The combination of the displacement of $-\text{X}$ by $-\text{OSO}_2\text{F}$, followed by conversion to an acyl fluoride or acid and decarboxylation, opens a path for stepwise fluorocarbon chain shortening.

EXPERIMENTAL

Volatile materials were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps, 316 stainless steel bellows seal valves and a Heise Bourdon tube-type pressure gauge. Transfers outside the vacuum line were carried out in a drybox. Infrared spectra were obtained using 5 cm path stainless steel cells with AgCl windows and a PE Model 283 spectrophotometer. Mass spectra were measured with an EAI Quad 300 quadrupole spectrometer and ^{19}F nmr spectra were determined with a Varian EM390 spectrometer operating at 84.6 MHz, using CFCl_3 as an internal standard. Chlorine fluorosulfate was prepared from

ClF and SO_3 [10]. Literature methods were used to synthesize $i\text{-C}_3\text{F}_7\text{X}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) [11], $\text{ClCF}_2\text{CF}_2\text{Cl}$ and $\text{CF}_3\text{CFClCF}_2\text{Cl}$ [12], $\text{BrCF}_2\text{CF}_2\text{CF}_2\text{Br}$ [13], and $\text{CF}_3\text{CFClCF}_2\text{SO}_3\text{F}$ [14]. Other fluorocarbon materials were purchased from PCR Research Chemicals, Inc.

R_fX Reactions. These reactions were carried out by loading measured quantities of the reactants, R_fX , chlorine fluorosulfate, and Br (where noted in Table I) into a precooled stainless steel cylinder. The reactions were allowed to proceed by warming the cylinder to a given temperature. Products were separated by fractional condensation and residual reactive impurities, such as XSO_3F or the halogens, were chemically removed by treatment with Hg. Table I summarizes the results from the reactions. Comparison to reported spectroscopic data served to identify most of the materials. Only new data and those for new compounds are presented herein.

$\text{FO}_3\text{SCF}_2\text{CF}_2\text{CF}_2\text{SO}_3\text{F}$. This compound was obtained from the reaction of $\text{BrCF}_2\text{CF}_2\text{CF}_2\text{Br}$ with ClSO_2F . Its ^{19}F nmr spectrum consisted of three peaks with an area ratio of 2:4:2 which are assigned to $-\text{SO}_3\text{F}$ (-50.8), terminal $-\text{CF}_2-$ (83.7), and internal $-\text{CF}_2-$ (128 ppm). The following infrared spectrum was observed (cm^{-1}) 1500(S), 1320(M), 1258(VS), 1220(S), 1150(S), 1127(S), 992(VS), 865(M), 843(VS), 752(M), 608(W), 570(M), and 548(M) which is similar to that of $\text{FO}_3\text{SCF}_2\text{CF}_2\text{SO}_3\text{F}$ [3]. Ions found in the mass spectrum were m/e (assign. rel. intens.) 249($\text{C}_3\text{F}_6\text{SO}_3\text{F}$, 1), 199($\text{C}_2\text{F}_4\text{SO}_3\text{F}$, 0.5), 169(C_3F_7 , 2), 150(C_3F_6 , 1), 149($\text{CF}_2\text{SO}_3\text{F}$, 8), 147($\text{C}_3\text{F}_5\text{O}$, 7), 119(C_2F_5 , 48), 100(C_2F_4 , 14), 97($\text{C}_2\text{F}_3\text{O}$, 2), 83(SO_2F , 100), 69(CF_3 , 15), 67(SOF , 6), 66(CF_2O , 1), 50(CF_2 , 1), 48(SO_2 , 4), 47(CFO , 27). In addition, this compound was characterized by its CsF catalyzed decomposition to 2 equivalents of SO_2F_2 and the corresponding acyl fluoride, OFCCF_2CFO . The latter was identified by comparison of its ^{19}F nmr, infrared, and mass spectra with literature values [15].

A by-product of the reaction of the dibromide with ClSO_3F was identified as $\text{ClCF}_2\text{CF}_2\text{CF}_2\text{SO}_3\text{F}$, based on its infrared spectrum (cm^{-1}) 1498(S), 1320(M), 1255(VS), 1233(S), 1190(S), 1118(M), 1078(S), 1024(S), 965(S), 843(S), 756(W), 595(W) and 560(W); and mass spectrum m/e (assign. rel. intens.) 249($\text{C}_3\text{F}_6\text{SO}_3\text{F}$, 0.3), 199($\text{C}_2\text{F}_4\text{SO}_3\text{F}$, 11), 185($\text{C}_3\text{F}_6\text{Cl}$, 3), 169(C_3F_7 , 25), 150(C_3F_6 , 20), 149($\text{CF}_2\text{SO}_3\text{F}$, 8), 147($\text{C}_3\text{F}_5\text{O}$, 3), 135($\text{C}_2\text{F}_4\text{Cl}$, 7).

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131(C₃F₅, 3), 119(C₂F₅, 49), 100(C₂F₄, 62), 97(C₂F₃O, 4), 85(CF₂Cl, 28), 83(SO₂F, 70), 69(CF₃, 100), 67(SOF, 10), 64(SO₂, 4), 51(SF, 2), 50(CF₂, 4), 48(SO, 4), and 47(CFO, 35). Assignments for Cl containing ions were confirmed by the presence of ³⁷Cl isotope ions of the expected one third intensity.

n-C₇F₁₅SO₃F. The reaction of n-C₇F₁₅I with a twofold excess of ClSO₃F was conducted at -45° because of the ease of oxidation of iodine by related hypochlorites [16]. At that temperature, one mole of Cl₂ was formed for each mole of R_fI and a white solid was produced. On warming to ambient temperature, the solid gradually decomposed furnishing the colorless liquid product, n-C₇F₁₅SO₃F and non-volatile ISO₃F. The infrared spectrum of n-C₇F₁₅SO₃F (cm⁻¹) 1505(S), 1336(W), 1258(VS), 1233(S), 1162(M), 1150(M), 1115(W), 1054(W), 1030(W), 868(M), 842(M), 760(W), 740(W), 730(W), 665(W) and 550(MW); and mass spectrum, m/e (assign. rel. intens.) 449(C₇F₁₄SO₃F, 0.3), 399(C₆F₁₂SO₃F, 0.1), 369(C₇F₁₅, 2), 347(C₇F₁₃O, 1), 319(C₆F₁₃, 1), 300(C₆F₁₂, 0.1), 281(C₅F₁₁, 2), 269(C₅F₁₁, 0.3), 247(C₅F₉O, 0.1), 231(C₅F₉, 2), 199(C₂F₄SO₃F, 0.1), 197(C₄F₇O, 0.3), 181(C₄F₇, 2), 169(C₃F₇, 9), 149(CF₂SO₃F, 13), 131(C₃F₅, 10), 119(C₂F₅, 18), 100(C₂F₄, 9), 97(C₂F₃O, 3), 83(SO₂F, 65), 80(SO₃, 4), 78(C₂F₂O, 1), 69(CF₃, 100), 67(SOF, 11), 64(SO₂, 8), 50(CF₂, 10), 48(SO, 9) and 47(CFO, 35) were used to identify the product. Additional proof was obtained by catalytically decomposing the fluorosulfate with CsF to furnish SO₂F₂ and C₆F₁₃CFO. The acyl fluoride was identified by infrared and mass spectra which included a parent ion.

[(i-C₃F₇)₂I]⁺[I(SO₃F)₄]⁻. Perfluoroisopropyl iodide and chlorine fluorosulfate reacted in a 1:2 mole ratio at -45° liberating one mole of Cl₂. The white, thermally stable, solid product of composition, i-C₃F₇I(SO₃F)₂, was formed in quantitative yield; from 2.36 mmol i-C₃F₇I was obtained 1.170 g solid (theory, 1.167 g), m.p. 101° (sealed tube). The Raman spectrum of the solid is shown in Figure 1.

R_fCO₂M. Prepassivated stainless steel cylinders were loaded in the drybox with measured amounts of R_fCO₂M (M=H, Na, Ag, or CF₃C=O). The halogen fluorosulfate XSO₃F (X=Cl or Br) was loaded into the cooled

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(-196°), evacuated cylinder from the vacuum line. After warming to a temperature of 25-50° for a given period, the products were separated by fractional condensation. Acid impurities, halogens, XSO_3F , and CO_2 when necessary, were removed from the products by treatment with aqueous base. All the products were identified spectroscopically and the data for new moieties are listed.

$\text{C}_7\text{F}_{15}\text{Cl}$. Sodium perfluorooctanoate was reacted with ClSO_3F for 2 days. In addition to CO_2 and solid NaSO_3F , the principle product was the colorless liquid $\text{C}_7\text{F}_{15}\text{Cl}$ whose identity was established from infrared (cm^{-1}) 1365(W), 1320(W), 1252(VS), 1223(S), 1160(M), 1121(W), 1072(W), 994(W), 780(W), 745(W), 706(W), 678(W), 650(W), 565(W), and 530(W); and mass spectra which did not exhibit a parent ion but had numerous peaks corresponding to $\text{C}_n\text{F}_{2n}^+$, $\text{C}_n\text{F}_{2n-1}^+$, and $\text{C}_n\text{F}_{2n}\text{Cl}^+$ with ($n=1-7$). A lesser quantity of the by-product $\text{C}_6\text{F}_{13}\text{ClO}$ was also formed and identified spectroscopically as noted earlier.

RESULTS AND DISCUSSION

As shown in Table I, this reaction can be carried out in high yields for Hal being Cl, Br, or I. The reactivity of the halogen decreases in the order $\text{I} > \text{Br} > \text{Cl}$ and is reflected by the necessary reaction temperatures. Whereas iodides react readily at temperatures as low as -45°, the chlorides require heating to about 130°. Furthermore, iodides react regardless of their position in the fluorocarbon molecules, i.e. as primary or secondary iodides. In the case of bromides and chlorides, only the primary halides were found to react, and in the case of the chlorides, even some of the primary chlorides were found to be unreactive. These unreactive chlorides included $\text{C}_2\text{F}_5\text{Cl}$, $\text{C}_7\text{F}_{15}\text{Cl}$, $\text{CF}_3\text{CFCICF}_3$, $\text{CF}_3\text{CFCICF}_2\text{Cl}$, $\text{ClCF}_2\text{CF}_2\text{SO}_3\text{F}$, and $\text{CF}_3\text{CFCICF}_2\text{SO}_3\text{F}$.

The reactivity of ClSO_3F can be enhanced by the addition of catalytic amounts of Br_2 , as demonstrated by examples 1, 3 and 4 of Table I. In the absence of bromine, only one chlorine atom is replaced by $-\text{SO}_3\text{F}$ in 1,2-dichloro-tetrafluoroethane, whereas in the presence of about 10% of Br_2 a significant amount of disubstitution is observed.

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Table 1. Fluorocarbon Halide Displacement Reactions

Reactant	mmol		Reactant	Temp. °C	Time Days	Products (%)
	ClSO_3F	Br_2				
$\text{ClCF}_2\text{CF}_2\text{Cl}$	6.42	-	3.10	130	5	$\text{ClCF}_2\text{CF}_2\text{SO}_3\text{F}$ (90) ^a
$\text{CF}_3\text{CF}_2\text{Cl}$	2.36	0.2	2.16	130	3	$\text{CF}_3\text{CF}_2\text{SO}_3\text{F}$ (22) ^a
$\text{ClCF}_2\text{CF}_2\text{Cl}$	11.8	0.6	5.94	140	1	$\text{ClCF}_2\text{CF}_2\text{SO}_3\text{F}$ (89) $\text{FO}_3\text{SCF}_2\text{CF}_2\text{SO}_3\text{F}$ (6) ^b
$\text{ClCF}_2\text{CF}_2\text{SO}_3\text{F}$	4.64	0.9	4.24	140	14	$\text{FO}_3\text{SCF}_2\text{CF}_2\text{SO}_3\text{F}$ (31)
$\text{CF}_3\text{CFCICF}_2\text{Cl}$	5.10	0.6	2.35	25	15	$\text{CF}_3\text{CFCICF}_2\text{SO}_3\text{F}$ (76) ^c
$\text{CF}_3\text{CF}_2\text{Br}$	5.31	-	4.98	25	21	$\text{CF}_3\text{CF}_2\text{SO}_2\text{F}$ (96)
$\text{BrCF}_2\text{CF}_2\text{Br}$	8.20	-	3.97	25	24	$\text{BrCF}_2\text{CF}_2\text{SO}_3\text{F}$ (40) ^a $\text{ClCF}_2\text{CF}_2\text{SO}_3\text{F}$ (5)
$\text{BrCF}_2\text{CF}_2\text{Br}$	4.75	-	2.18	65	2	$\text{FO}_3\text{SCF}_2\text{CF}_2\text{SO}_3\text{F}$ (64) $\text{ClCF}_2\text{CF}_2\text{SO}_3\text{F}$ (31)
$\text{Br}(\text{CF}_2)_3\text{Br}$	5.16	-	2.04	50	11	$\text{FO}_3\text{SCF}_2\text{CF}_2\text{CF}_2\text{SO}_3\text{F}$ (50) $\text{ClCF}_2\text{CF}_2\text{CF}_2\text{SO}_3\text{F}$ (10)
$\text{CF}_3\text{CFBrCF}_2\text{Br}$	4.78	-	2.15	25	21	$\text{CF}_3\text{CFBrCF}_2\text{SO}_3\text{F}$ (70) ^c
$n\text{-C}_7\text{F}_{15}\text{I}$	6.05	-	2.73	25	7	$n\text{-C}_7\text{F}_{15}\text{SO}_3\text{F}$ (85)
$\text{CF}_3\text{CFICF}_3$	5.20	-	2.34	-45	10	$[(i\text{-C}_3\text{F}_7)_2\text{I}]^+$ $[\text{I}(\text{SO}_3\text{F})_4]^-$

100

- a) Ref. 4
b) Ref. 3
c) Ref. 14

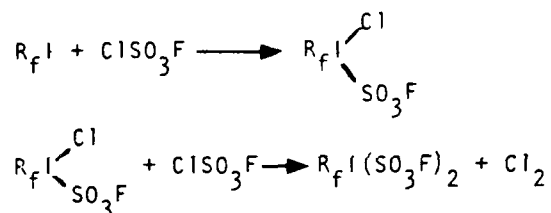
Additional cases showing the catalytic effect of Br_2 are examples 2 and 5 of Table 1. However, the secondary halides in $\text{CF}_3\text{CFBrCF}_3$ and $\text{CF}_3\text{CFCICF}_2\text{SO}_3\text{F}$ were found to be unreactive even in the presence of Br_2 . An isolated example of the displacement of secondary Br with $\text{S}_2\text{O}_6\text{F}_2$ is known [17], but in that instance it was adjacent to a carbonyl group, $\text{CF}_3\text{CFBrC(O)CF}_3$. Interestingly, Fokin [7] reported that one of the

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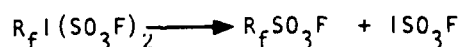
chlorines of the CFCl_2 group in $\text{ClCF}_2\text{CFCl}_2$ is replaced by SO_3F using ClSO_3F , but that the reaction requires HSO_3F catalysis. While we cannot be absolutely certain that no HSO_3F was present in our system, all efforts were made to exclude moisture. In addition it should be noted that the above fluorosulfate substitution reactions do not result in any C-C bond breakage and also that ether functions are not affected [18].

The catalytic effect of bromine is best explained by the in situ generation of the more reactive BrSO_3F from Br_2 and ClSO_3F . Since the generated HalBr species are generally unstable and decompose back to Br_2 , only catalytic amounts of bromine are required.

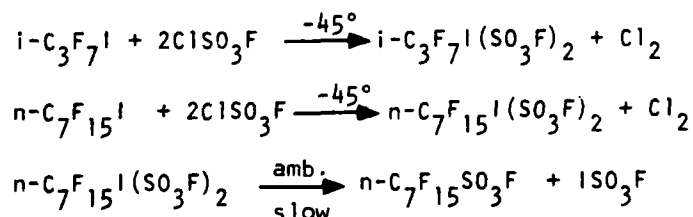
By analogy with the known reaction chemistry of other positive halogen compounds [16], fluorocarbon iodides and ClSO_3F were expected to undergo an oxidative addition, followed by $-\text{SO}_3\text{F}$ substitution



This compound may then undergo ISO_3F elimination



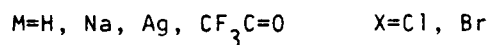
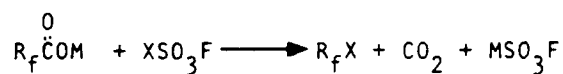
Depending on the thermal stability of the $\text{R}_f\text{I}(\text{SO}_3\text{F})_2$ intermediate, either this intermediate or the final $\text{R}_f\text{SO}_3\text{F}$ product was obtained. The formation of $\text{R}_f\text{SO}_3\text{F}$ from this reaction had already previously been established for CF_3I [6,7]. The fact that this reaction indeed proceeds through the above intermediate has now been demonstrated for both n-perfluoroheptyl iodide and perfluoroisopropyl iodide:



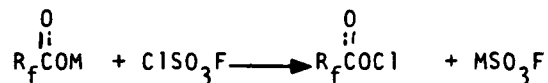
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Thus for the heptyl case, a clearly defined two-step substitution process was noted. For the isopropyl case, the oxidative addition product was stable even at its melting point, 101°. Examination of its Raman spectrum (Figure 1) showed that this solid adduct is not a covalent iodine (III) compound, but has instead the ionic structure $[(i-C_3F_7)_2I]^+[I(SO_3F)_4]^-$. Thus, these $R_fI-ClSO_3F$ reactions and products are analogous to those previously reported for $R_fI-ClOClO_3$ systems [19].

With carboxylic acids their salts, or anhydrides, $ClSO_3F$ or $BrSO_3F$ acted at ambient temperature or slightly above as a most facile decarboxylating agent (Table 2).



High yields of R_fX were generally encountered. Where lower, the observed decrease was probably caused by either a lower purity starting material (used as received) or a side reaction such as the decarboxylation giving CF_2Cl_2 which reacted further to furnish $ClCF_2SO_3F$, a known interaction [20]. The $R_fCO_2M + XSO_3F$ reactions probably proceed through the intermediate formation of R_fCO_2X . When the $R_fCO_2M-ClSO_3F$ system is moderated sufficiently, i.e. by lowering the temperature to -45° or lower, then the intermediate acyl hypochlorite, R_fCO_2Cl , may be isolated [21].



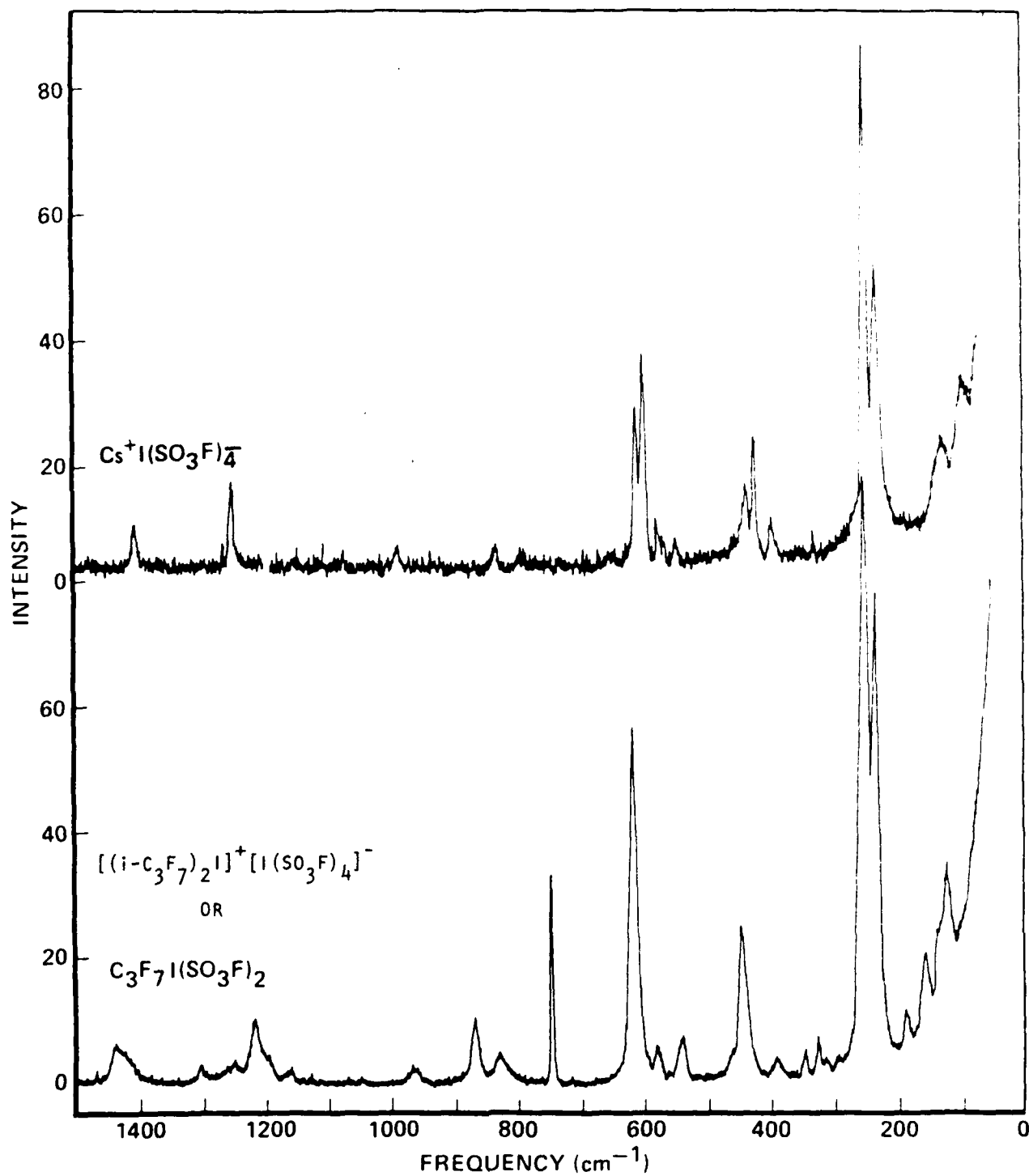


Figure 1. Raman Spectra of $\text{Cs}^+\text{I}(\text{SO}_3\text{F})_4^-$ and $[(i-\text{C}_3\text{F}_7)_2\text{I}]^+[\text{I}(\text{SO}_3\text{F})_4]^-$ Demonstrating the presence of the $\text{I}(\text{SO}_3\text{F})_4^-$ Anion in the Latter Compound

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Table 2. Fluorocarbon Acid and Derivative Reactions^a

Reactant	mmol	X-SO ₃ F	mmol	Time(hr)	Products ()
CF ₃ CO ₂ H	4.30	Cl	4.30	5	CF ₃ Cl (90)
CF ₃ CO ₂ H	2.46	Br	2.31	2	CF ₃ Br (88)
ClCF ₂ CO ₂ H	2.80	Cl	2.91	3	CF ₂ Cl ₂ (85)
CF ₂ (CF ₂ CO ₂ H) ₂	2.29	Cl	4.86	18	CF ₂ (CF ₂ Cl) ₂ (86) ^b , ClCF ₂ CF ₂ CFO (11), ClCF ₂ CF ₂ CF ₂ SO ₃ F (1)
CF ₃ CF ₂ CO ₂ Na	2.82	Cl	2.66	24	CF ₃ CF ₂ Cl (79), CF ₃ CF ₂ SO ₃ F (2)
CF ₃ CF ₂ CO ₂ Na	2.54	Br	2.76	5	CF ₃ CF ₂ Br (83)
C ₇ F ₁₅ CO ₂ Na	2.26	Cl	2.19	48	C ₇ F ₁₅ Cl (78), C ₆ F ₁₃ CFO (18)
CF ₂ (CF ₂ CO ₂ Ag) ₂	2.38	Cl	4.94	48	CF ₂ (CF ₂ Cl) ₂ (53), ClCF ₂ CF ₂ CFO (8), CF ₃ CF ₃ CF ₂ Cl (3)
ClCF ₂ CO ₂ Na	2.11	Cl	2.59	48	CF ₂ Cl ₂ (28), ClCF ₂ SO ₃ F (39) ^c , ClCF ₂ CFO (1)
(CF ₃ CO) ₂ O	2.43	Cl	2.42	24	CF ₃ Cl (80), CF ₃ C(O)SO ₃ F (85) ^d

a) Reactions generally run at ambient temperature although some were also heated at 50° for a short period

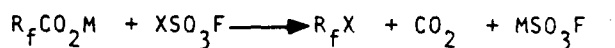
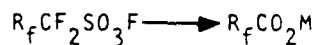
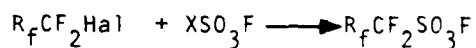
b) Ref. 12.

c) Ref. 20.

d) Ref. 8.

SUMMARY

The above results show that ClSO_3F and BrSO_3F are useful reagents for introducing a functional $-\text{SO}_3\text{F}$ group into the generally unreactive class of fluorocarbon halides and to convert fluorocarbon carboxylic acids to the corresponding fluorocarbon halides. A combination of both reactions offers a unique, high yield method to carry out a chain shortening reaction for the otherwise highly "inert" fluorocarbon halides according to



Since the chain shortening product is a fluorocarbon halide, the shortening cycle can be repeated as often as desired.

ACKNOWLEDGEMENT

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APPENDIX E

IODINE FLUOROSULFATE REACTIONS WITH FLUOROCARBONS

IODINE FLUOROSULFATE REACTIONS WITH FLUOROCARBONS

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ABSTRACT

Iodine monofluorosulfate has been found to react with fluoroolefins in the absence of a solvent to give the corresponding iodo alkyl fluorosulfates by addition of $-I$ and $-OSO_2F$ across the double bond. The observed order of reactivity was $CF_2=CF_2 > CF_3CF=CF_2 > CF_2=CFCl$ with perfluorocyclobutene being unreactive. The observed products were $ICF_2CF_2SO_3F$, $CF_3CFICF_2SO_3F$, and the isomer mixture $ICF_2CFCISO_3F$ and $ICFCICF_2SO_3F$. The iodine fluorosulfate used for this study was synthesized from the reactions of either I_2 or R_fI with $ClSO_3F$, with both reactions being new routes to this compound. These iodo fluorocarbon fluorosulfates are novel compounds and were characterized by spectroscopy and by formation of the derivatives $CF_3CFICFO$ and ICF_2CFO .

INTRODUCTION

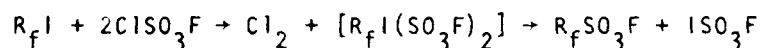
The halogen fluorosulfates are very reactive materials in general, being capable of oxidation or substitution processes in either organic or inorganic systems [1]. One of the earliest reactions described was the addition of XSO_3F to carbon-carbon double bonds [2] where $X=F, Cl, \text{ or } Br$. However, despite the fact that iodine monofluorosulfate became known at about the same time [3], no reports on similar reactions of $IOSO_2F$ have appeared. Indeed, the chemistry of $IOSO_2F$ (commonly written, ISO_3F) and

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$\text{I}(\text{SO}_3\text{F})_3$ is practically non-existent [1,4] and no organic derivatives have been reported.

In a previous study [5] of fluorocarbon halide-chlorine fluorosulfate displacement reactions the following products were noted.



Based on the observed material balance, the by-product iodine fluorosulfate was formed in nearly quantitative yield, but was identified only by its physical appearance, i.e. a black solid at ambient temperature [3]. Thus having samples of ISO_3F readily available, it was interesting to determine whether this compound would be useful for the preparation of simple organic derivatives. We now report the results of experiments utilizing olefins.

EXPERIMENTAL

Volatile materials were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps, 316 stainless steel bellows seal valves and a Heise Bourdon tube-type pressure gauge. Transfers outside the vacuum line were carried out in a drybox. Infrared spectra were obtained using 5 cm path stainless steel cells with AgCl windows and a PE Model 283 spectrophotometer. Mass spectra were measured with an EAI Quad 300 quadrupole spectrometer and ^{19}F nmr spectra were determined with a Varian EM390 spectrometer operating at 84.6 MHz, using CFCl_3 as an internal standard. Chlorine fluorosulfate was prepared from ClF and SO_3 [6]. The fluorocarbon starting materials were purchased from PCR Research Chemicals, Inc., and used as received.

ISO_3F Preparations

A 30 ml stainless steel cylinder was loaded with I_2 (4.02 mmol) and ClSO_3F (8.09 mmol) and maintained at -78° overnight followed by a day at -45° . While warming to ambient temperature the volatile products were pumped from the cylinder and trapped at -196° . These consisted of Cl_2 and a trace of ClSO_3F (4.02 mmol total) indicating an essentially quantitative

reaction of the ClSO_3F . The weight increase of the cylinder corresponded to that expected for the formation of ISO_3F . When this reaction was carried out in a Teflon ampoule, it was noted that the solid product was orange at low temperatures and only changed to the black color typical ISO_3F on standing at 0° or higher for some time.

An alternative preparation of ISO_3F used in this study was the reaction of R_fI with ClSO_3F . Thus, $n\text{-C}_3\text{F}_7\text{I}$ (2.90 mmol) and ClSO_3F (6.16 mmol) were combined in a stainless steel cylinder and maintained at -45° for several days. While warming to ambient temperature the volatile products were separated by fractional condensation in traps cooled to -45° , -78° and -196° . The latter contained Cl_2 (2.91 mmol) and a little $\text{C}_3\text{F}_7\text{SO}_3\text{F}$ and $\text{C}_3\text{F}_7\text{I}$. The warmer traps contained only $\text{C}_3\text{F}_7\text{SO}_3\text{F}$ (2.77 mmol) in 95% yield. Iodine fluorosulfate remained in the cylinder, however, the observed weight (0.682g) was somewhat higher than the theoretical weight (0.656g) possibly due to the formation of some $\text{I}(\text{SO}_3\text{F})_3$ as an impurity.

$\text{CF}_3\text{CFICF}_2\text{SO}_3\text{F}$

To the ISO_3F (2.90 mmol) formed from $\text{C}_3\text{F}_7\text{I}$ and ClSO_3F was added $\text{CF}_3\text{CF}=\text{CF}_2$ (2.40 mmol) at -196° . The mixture was allowed to react by warming the cylinder to room temperature for several days. The only volatile product was $\text{CF}_3\text{CFICF}_2\text{SO}_3\text{F}$ (2.35 mmol, 98% yield), a colorless liquid with a vapor pressure of 13 mm at 25° . This liquid was identified by its; ^{19}F NMR, infrared, and mass spectra. IR, cm^{-1} (intens.): 1494 (vs), 1262 (vs), 1232 (vs), 1190 (VW), 1115 (s), 979 (s), 962 (sh), 924 (w), 905 (m), 846 (s), 764 (m), 727 (w), 611 (vw), 574 (m), and 537 (vw). Intense ions found in the mass spectra were m/e (assign.): 376 ($\text{C}_3\text{F}_6\text{ISO}_3\text{F}$), 277 ($\text{C}_3\text{F}_6\text{I}$), 249 ($\text{C}_3\text{F}_6\text{SO}_3\text{F}$), 150 (C_3F_6), 149 ($\text{CF}_2\text{SO}_3\text{F}$), 131 (C_3F_5), 127 (I), 100 (C_2F_4), 83 (SO_2F), 69 (CF_3 , base), 67 (SOF), 64 (SO_2), 50 (CF_2), 48 (SO), and 47 (CFO).

$\text{ICF}_2\text{CF}_2\text{SO}_3\text{F}$

A cylinder containing ISO_3F (6.56 mmol), prepared from I_2 and ClSO_3F , was cooled to -196° and C_2F_4 (7.05 mmol) was added. The cylinder was placed

in a liquid nitrogen/CO₂ slush and allowed to warm slowly to ambient temperature. After a few days the volatile products were pumped through traps cooled at -30, -78, and -196°. The latter contained a mixture (0.25 mmol) of ClCF₂CF₂SO₃F [2], Cl₂, and an unidentified acyl fluoride. The -30° fraction contained small amounts of FO₃SCF₂CF₂SO₃F [7] and ICF₂CF₂SO₃F while the -78° fraction was good quality ICF₂CF₂SO₃F (3.98 mmol, 61% yield) colorless liquid with a vapor pressure of 24 mm at 22°. The remaining unaccounted for reactants were found in the cylinder in the form of a white solid polymer and dark oil, presumably I(C₂F₄)_nSO₃F, I(C₂F₄)_nI, or FO₃S(C₂F₄)_nSO₃F type materials which were not examined further. The ISO₃F - C₂F₄ reaction was repeated using ISO₃F (3.41 mmol) which was the 2 year old by-product of a C₇F₁₅I - ClSO₃F reaction [5]. Together with C₂F₄ (3.96 mmol) and a more controlled warm-up, this reaction produced a yield of purified ICF₂CF₂SO₃F of 76% based on ISO₃F: vapor density obs'd. 330; calc'd. 326g/mol. Spectral characterization included infrared, cm⁻¹ (intens.); 1497 (vs), 1301 (ms), 1262 (vs), 1226 (ms), 1167 (s), 1147 (s), 1105 (s), 1080 (s), 952 (ms), 931 (ms), 845 (s), 792 (m), 600 (w), and 555 (w); mass spectra, m/e (assign.): 326 (C₂F₄ISO₃F), 227 (C₂F₄I), 199 (C₂F₄SO₃F), 177 (CF₂I), 158 (CFI), 149 (CF₂SO₃F), 127 (I), 119 (C₂F₅), 100 (C₂F₄), 97 (C₂F₃O), 83 (SO₂F, base) 81 (C₂F₃), 69 (CF₃), 67 (SOF), 64 (SO₂), 50 (CF₂), 48 (SO) and 47 (CFO); and ¹⁹F NMR spectra (Table 1).

ICF₂CFClSO₃F — ICFClCF₂SO₃F

A cylinder containing ISO₃F (4.02 mmol) prepared from I₂ and ClSO₃F was cooled to 0° and CF₂=CFCl (8.12 mmol) was gradually added with intermittent shaking and keeping the pressure below 300 mm. After the first half of the olefin was added the uptake of CF₂=CFCl became slow. Consequently, the final 2 mmol was condensed at -196° into the cylinder and the mixture kept at ambient temperature overnight. Fractional condensation through traps cooled at 0, -30, -78, and -196° served to separate unreacted CF₂=CFCl (1.22 mmol) retained at -196°, and I₂ (a few crystals) retained at 0°. The other two traps contained a slightly purplish liquid which was recombined and treated with Hg to remove I₂ and refractionated through 0, -30, and -78°. The -78° material (0.5 mmol) was mainly ClCF₂CFClSO₃F based on its infrared

and ^{19}F NMR spectra [8]. The 0 and -30° fractions (6.40 mmol total, 79.6% yield) were colorless liquids with quite similar infrared, mass, and NMR spectra. The latter showed clearly that three compounds were present in the mixture; $\text{ICF}_2\text{CFCISO}_3\text{F}$, $\text{ICFCICF}_2\text{SO}_3\text{F}$, and $\text{FO}_3\text{SCFCICF}_2\text{SO}_3\text{F}$. Based on the measured peak areas, the ratio of the first two isomeric materials was 1.5 and they comprised 95% of the sample. The infrared spectrum of the isomers was recorded, cm^{-1} (intens.): 1491 (vs), 1306 (vw), 1253 (vs), 1219 (m), 1167 (s), 1134 (s), 1080 (s), 1058 (s), 1010 (m), 987 (m), 945 (w), 927 (w), 860 (sh), 842 (vs), 780 (m), 700 (w), and 569 (m). Intense ion peaks noted in the mass spectrum were m/e (assign.) (^{35}Cl only given): 342 ($\text{C}_2\text{F}_3\text{ClISO}_3\text{F}$), 243 ($\text{C}_2\text{F}_3\text{ClI}$), 215 ($\text{C}_2\text{F}_3\text{ClISO}_3\text{F}$), 193 (CFCI), 177 (CF_2I), 165 (CFCISO_3F), 149 ($\text{CF}_2\text{SO}_3\text{F}$), 127 (I), 116 ($\text{C}_2\text{F}_3\text{Cl}$), 113 ($\text{C}_2\text{F}_3\text{ClO}$), 97 ($\text{C}_2\text{F}_3\text{O}$), 85 (CF_2Cl), 83 (SO_2F , base), 69 (CF_3), 67 (SOF), 66 (CFCI), 64 (SO_2), 63 (CClO), 50 (CF_2), 48 (SO), and 47 (CFO). The ^{19}F NMR spectra are listed in Table 1.

CF_3CFICFO

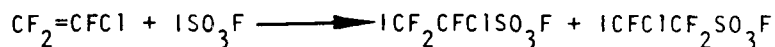
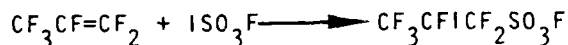
A 30 ml stainless steel cylinder containing CsF (1.24g) and $\text{CF}_3\text{CFICF}_2\text{SO}_3\text{F}$ (1.12 mmol) was placed in an oven at 100° for 1 hour. The products volatile at 25° were removed from the cylinder by pumping and were found to be SO_2F_2 (1.2 mmol) with traces of R_f - material. Pyrolysis of the solid left in the cylinder (heat gun, 15 min.) while pumping through a -196° trap yielded CF_3CFICFO (1.03 mmol, 92% yield). This compound was identified by its vapor density; obs'd. 271g/mol, calc'd. 274g/mol and spectral parameters. Infrared bands were, cm^{-1} (intens.): 1862 (vs), 1278 (vs), 1256 (vs), 1211 (vs), 1117 (s), 974 (w), 954 (m), 886 (m), 755 (w), and 683 (m). The intense mass fragments were, m/e (assign.): 274 ($\text{C}_3\text{F}_5\text{IO}$), 227 ($\text{C}_2\text{F}_4\text{I}$), 177 (CF_2I), 147 ($\text{C}_3\text{F}_5\text{O}$), 128 ($\text{C}_3\text{F}_4\text{O}$), 127 (I), 119 (C_2F_5), 100 (C_2F_4), 97 ($\text{C}_2\text{F}_3\text{O}$), 81 (C_2F_3), 69 (CF_3 , base), 50 (CF_2), and 47 (CFO). The ^{19}F NMR spectrum is listed in Table 1.

ICF₂CFO

A mixture of ICF₂CF₂SO₃F (0.42 mmol) and CsF was heated at 100° for 2 hours. Recooling to room temperature and fractionation of the volatile products through traps cooled at -126 and -196° permitted the separation of SO₂F₂ and traces of R_fCFO from ICF₂CFO (0.38 mmol, 91.3% yield) which was retained at -126°. The observed infrared bands were, cm⁻¹ (intens.): 1870 (vs), 1243 (vs), 1175 (s), 1083 (vs), 901 (s), 842 (w), and 645 (m). The ¹⁹F NMR spectrum is listed in Table 1.

RESULTS AND DISCUSSION

Iodine monofluorsulfate was found to add across olefinic double bonds according to:



The observed order of reactivity was C₂F₄ > C₃F₆ > C₂F₃Cl with the tetrafluoroethylene reaction sometimes being quite vigorous, resulting in oily or solid polymer formation. The chlorotrifluoroethylene reaction, however, required little moderation and proceeded at a rather slow rate after about half the available ISO₃F was consumed. The least reactive olefin was perfluorocyclobutene which did not react with ISO₃F under comparable conditions although it does add ClSO₃F readily to give C-C₄F₆Cl(SO₃F). [6]. The reactions of ISO₃F with the above olefins occur in yields of 76-98% in agreement with the anticipated 1:1 stoichiometry. All of the products are mobile, colorless liquids of low volatility.

Measurement of the spectral properties of the products confirmed their identity. The formulation as I-R_f-SO₃F adducts was confirmed by the mass spectra which in all cases exhibited a readily detectable m/e peak attributable to the expected parent ion. This is in agreement with general observations for iodo fluorocarbons. The other mass fragments support the formulated structures. Noteworthy is the fact that m/e 83, attributable to the SO₂F⁺ ion, constitutes the base peak in those fluorosulfates lacking a

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INORGANIC REACTANTS FOR SYNTHESIS OF NOVEL FLUOROCARBON DERIVAT--ETC(11)
MAY 80 C J SCHACK, K O CHRISTE P#9620-77-C-0038
RI/RD80-152 AFOSR-TR-80-0450 NL

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a CF_3^- group. In the latter case, m/e 69 due to CF_3^+ is the peak. The infrared spectra of these compounds show the bands characteristic for a monodentate SO_3F group ($\sim 1500\text{ cm}^{-1}$, vs, vas SO_2 ; $\sim 850\text{ cm}^{-1}$ S-O, S-F stretch). In addition to the expected strong C-F stretching modes there are moderately strong bands in the $900\text{-}1000\text{ cm}^{-1}$ region due to both C-C and C-O stretching vibrations.

Table 1. ^{19}F Chemical Shifts^a and Coupling Constants^b

	CF_3	CFI	CF_2	CFCI	CF_2	SO_3F	$J_{\text{FF}}(\text{Hz})$
$\text{ICF}_2\text{CF}_2\text{SO}_3\text{F}$			64.8		85.3	-48.6	$J_{12}^{4.7}, J_{23}^{8.0}$
$\text{ICF}_2\text{CFCISO}_3\text{F}$			58.5	72.8		-49.6	$J_{12}^{9.4}, J_{23}^{9.4}$
$\text{ClCF}_2\text{CFCISO}_3\text{F}$			69.0	75.8		-48.9	$J_{12}^{5.6}, J_{23}^{9.6}$
$\text{FO}_3\text{SCFCICF}_2\text{SO}_3\text{F}$				79.7	86.1	-50.6	$J_{12}^{8.0}, J_{23}^{3.4}$
						-49.4	$J_{34}^{8.2}$
$\text{ICFCICF}_2\text{SO}_3\text{F}$				78.0	82.3	-48.4	$J_{12}^{11.8}, J_{22}^{9.3}$
							$J_{23}^{8.2}$
$\text{CF}_3\text{CFICF}_2\text{SO}_3\text{F}$	74.8	148.6			77.5	-48.1	$J_{12}^{11.8}, J_{13}^{9.4}$
							$J_{22}^{11.8}, J_{34}^{8.1}$
ICF_2CFO			59.8				$J_{12}^{3.7}$
						-7.8	
CF_3CFICFO	76.9	142.9				-19.6	$J_{12}^{12.3}, J_{13}^{8.8}$
							$J_{23}^{26.8}$

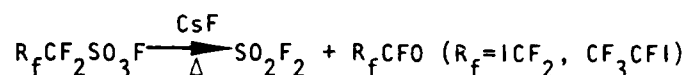
^a Ppm upfield from internal CFCI_3 . The observed area ratios, multiplicities and coupling constants verified the above assignments.

^b The subscripts of the coupling constants refer to the sequence of the carbon or sulfur atoms in the molecular structures given in the first column of the table and increase from left to right.

Definitive results regarding the structure of the compounds was furnished by their ^{19}F NMR spectra which are summarized in Table 1. These data, when

compared to literature values [9] for similar compounds, are very characteristic. The $-\text{SO}_3\text{F}$ fluorine shift is always near -49 ppm, while other carbon-fluorine groups exhibit well established and distinct chemical shifts. It is noteworthy that the isomer $\text{ICFClCF}_2\text{SO}_3\text{F}$ shows hindered rotation about the C-C bond up to at least 80° as evidenced by the magnetic non-equivalence ($\Delta\nu=9.3\text{Hz}$) of the two fluorines of the CF_2 resonance. This is often found for similar ethane derivatives [10].

Two of the new fluorocarbon fluorosulfates were catalytically decomposed as shown in the equation.



These high yield reactions are very useful in furnishing a derivative for identification of the parent compound [5,11]. The acyl fluorides obtained were characterized in the same manner as the fluorosulfates.

Overall these reactions of ISO_3F and olefins resemble those of ClSO_3F [12]. Thus, $\text{CF}_3\text{CF}=\text{CF}_2$ gives only the one isomer expected for a directed polar addition, while $\text{CF}_2=\text{CFCl}$ gives two, even though both systems might be expected to proceed by the same reaction path [13]. Steric factors cannot be important in these cases since the double bonds are not sufficiently hindered to account for the difference. Thus, a single mechanism to explain this behavior is not readily apparent. Nevertheless, it has been shown that potentially useful organic derivatives of ISO_3F can be easily made. Additional studies of ISO_3F reactions are planned. Also it should be mentioned that INO_3 , generated in solution as a pyridinium salt, has recently been successfully added to unsaturated hydrocarbon substrates [14].

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APPENDIX F

SUBSTITUTION AND ADDITION REACTIONS OF NF_4BF_4 WITH AROMATIC COMPOUNDS

SUBSTITUTION AND ADDITION REACTIONS OF NF_4BF_4 WITH AROMATIC COMPOUNDS

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ABSTRACT

Benzene, toluene, and nitrobenzene interact rapidly with NF_4BF_4 in anhydrous HF to give, almost exclusively, fluorine substituted aromatic derivatives. With benzene, up to five hydrogens were replaced, while a maximum of four hydrogens were displaced in $\text{C}_6\text{H}_5\text{CH}_3$ and $\text{C}_6\text{H}_5\text{NO}_2$. Numerous mono and difluoro derivatives were also formed with mainly ortho and para F for toluene and meta F for nitrobenzene in agreement with an electrophilic substitution mechanism. Very little loss of CH_3 or NO_2 substituents occurred and the CH_3 group was not fluorinated. The highly fluorinated aromatic compounds C_6F_6 , $\text{C}_6\text{F}_5\text{H}$, and $p\text{-C}_6\text{F}_4\text{H}_2$, reacted much slower with NF_4BF_4 in HF, even at room temperature. During these reactions, almost no hydrogen substitution occurred, but addition of 2 or 4 fluorines to the ring took place. The addition of the first pair of fluorines always gave 1, 4-cyclohexadienes in which the >CF_2 group was ortho to hydrogen on the ring. The addition of the second pair of fluorines resulted in the formation of cyclohexenes. These reactions occurred in high yield and the products were characterized spectroscopically and by comparison to literature data.

INTRODUCTION

The known methods for introducing fluorine into an aromatic ring are limited [1]. Classically the Balz-Schiemann has been used for step-wise

introduction of F, while more recently XeF_2 [2] and CF_3OF [3] have been widely investigated. Although capable of very specific fluorination in some cases these two compounds have a limited degree of reactivity and are not useful for multiple fluorine substitution. When highly fluorinated aromatic compounds are desired, the approach has been to use metal fluorides at elevated temperature in an exhaustive fluorination leading to saturated compounds. These are then rearomatized by defluorination or dehydrofluorination reactions. Since substituents on the ring are either fluorinated, e.g. $\text{CH}_3 \rightarrow \text{CF}_3$ or displaced, it is necessary to reintroduce required substituents through additional reactions. Clearly there is a need for vigorous, yet selective, reagents which can directly introduce fluorine into aromatic compounds. Being aware of the highly reactive nature of NF_4^+ salts by reason of several year's of work with them in these laboratories [4,5], and yet knowing that these salts are very tractable under the proper conditions, an investigation was begun into their usefulness for substituting fluorine into aromatic rings. We now report the results of our initial screening of NF_4BF_4 in reactions with simple aromatic hydrocarbons; C_6H_6 , $\text{C}_6\text{H}_5\text{CH}_3$, and $\text{C}_6\text{H}_5\text{NO}_2$; and also with highly fluorinated aromatics; C_6F_6 , $\text{C}_6\text{F}_5\text{H}$ and p- $\text{C}_6\text{F}_4\text{H}_2$.

EXPERIMENTAL

Volatile materials were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps, 316 stainless steel bellows seal valves and a Heise Bourdon tube-type pressure gauge. Hydrogen Fluoride work was carried out in an all Monel and Teflon vacuum system. Transfers outside the vacuum line were carried out in a drybox. Infrared spectra were obtained using 5 cm path stainless steel cells with AgCl windows and a PE Model 283 spectrophotometer. Mass spectra were measured with an EAI Quad 300 quadrupole spectrometer and ^{19}F nmr spectra were determined with a Varian EM390 spectrometer operating at 84.6 MHz, using TMS or CFCl_3 as an internal standards. Positive chemical shifts are upfield from CFCl_3 and downfield from TMS. Raman spectra were recorded on a Cary Model 283 using the 4880 Å exciting line. Gas chromatographic data were obtained using a Varian GC under isothermal conditions (135°) with a stainless steel column (1/8" X 10') packed with Poropak PS. The solid NF_4BF_4 was prepared

from $\text{NF}_3\text{-F}_2\text{-BF}_3$ at low temperature using UV activation, which gives essentially pure material [4].

NF_4BF_4 Reactions With Aromatics

C₆F₆. A sample of NF_4BF_4 (4.07 mmol) contained in a Teflon (FEP) ampoule was dissolved in anhydrous HF (4 ml) and cooled to -78° : Hexafluorobenzene (1.25 mmol) was condensed into the ampoule which was then warmed gradually while stirring magnetically. After being overnight at $0\text{-}10^\circ$, the clear, colorless solution was cooled to -78° and the volatile material quickly removed by passing to a -196° trap. The -196° trap contained NF_3 (1.24 mmol) contaminated with traces of HF as shown by an infrared spectrum. The reaction was allowed to continue another day at room temperature. While maintaining the reaction ampoule at 0° , the volatile products and HF were separated by fractional condensation in a series of U-traps cooled at -45 , -78 , and -196° . The -196° fraction, NF_3 and HF, was discarded and the -45° trap was empty. The -78° trap contained a white solid, which melted to a colorless liquid above 0° . Examination of this material by infrared [6] and gas chromatography showed it to be 1, 4 perfluorocyclohexadiene (1.18 mmol, 94.3% yield) with a slight amount (2-3%) of unreacted C_6F_6 . Intense ions in the mass spectrum were observed at m/e (assign.): 224 (C_6F_8), 205 (C_6F_7), 186 (C_6F_6), 174 (C_5F_6), 155 (C_5F_5 , base), 136 (C_5F_4), 124 (C_4F_4), 117 (C_5F_3), 105 (C_4F_3), 93 (C_3F_3), 86 (C_4F_2), 74 (C_3F_2), 69 (CF_3), 55 (C_3F), and 31 (CF). The ^{19}F NMR spectrum showed two equal area multiplets at 113.1 and 158.3 ppm in agreement with the literature [7] for 1,4- C_6F_8 . A white solid remained in the reaction ampoule and it was shown by Raman spectroscopy [4] to be NF_4BF_4 (1.48 mmol).

C₆F₅H. As in the preceding example, NF_4BF_4 (4.29 mmol) in HF with added $\text{C}_6\text{F}_5\text{H}$ (1.35 mmol) was stirred and warmed from -78° for several hours and then at room temperature overnight. Evolved NF_3 was monitored and about 3.3 mmol was noted. Several more hours stirring at room temperature was followed by vacuum fractionation through U-traps cooled at -45 , -78 , and -196° . All material passed the -45° trap except for a small amount of

NF_4BF_4 remaining in the reactor. The -196° fraction was discarded. The -78° trap contained 1.24 mmol of a colorless liquid whose infrared spectrum indicated that it was composed of more than one cyclohexene [1770 (ms), 1740 (s), and 1720 cm^{-1} (vs)] as well as unreacted $\text{C}_6\text{F}_5\text{H}$. Gas chromatography showed three components which were analyzed individually by mass spectroscopy. In order of elution they were; (1) 1, 4- C_6F_8 , 26.1% (2), 1H-heptafluorocyclohexa -1, 4-diene, 66.3%, and (3) $\text{C}_6\text{F}_5\text{H}$, 7.6%. The mass spectra of the fractions agreed very well with published data [8] for the assigned compounds. In addition, the ^{19}F NMR spectra confirmed the formulated structures. For 1-H heptafluorocyclohexa -1, 4-diene, a literature report of the NMR spectrum was not found, but by comparison with related compounds [9, 10] it was apparent that the observed resonances and area ratios were reasonable for that structure, position of H or F, ppm or δ (rel. F area): 1-H, 5.93; 2-F, 127.7 (1); 3-F, 115.2 (2); 4-F, 160 (1); 5-F, 155 (1), 6-F, 101.7 (2). Only 8% of the $\text{C}_6\text{F}_5\text{H}$ was recovered unchanged. Of the reacted material, 25% was obtained as 1, 4- C_6F_8 and 65% as 1, 4- $\text{C}_6\text{F}_7\text{H}$. The balance was not accounted for.

p- $\text{C}_6\text{F}_4\text{H}_2$. A mixture of NF_4BF_4 (4.18 mmol) and p- $\text{C}_6\text{F}_4\text{H}_2$ (1.43 mmol) in 4 ml HF at -78° was stirred and warmed to 0° over 3 hours, followed by overnight stirring at $0-20^\circ$. Fractional condensation at -78° and -196° was used to separate HF and NF_3 from the products which were retained in the -78° trap. No unreacted NF_4BF_4 remained in the reactor. The original -78° fraction was further separated by refractioning through -45 and -78° traps. The former contained 0.21 mmol of a colorless liquid whose infrared spectrum showed a strong band at 1710 cm^{-1} typical for the double bond of a $-\text{CF}=\text{CH}-$ group. Analysis using GC/MS procedures showed this material to be 1H, 4H-hexafluorocyclohexa -1, 4-diene [11]. Prominent mass spectral peaks were found at m/e (assign.): 188 ($\text{C}_6\text{F}_6\text{H}_2$), 169 ($\text{C}_6\text{F}_7\text{H}_2$), 150 ($\text{C}_6\text{F}_4\text{H}_2$), 138 ($\text{C}_5\text{F}_4\text{H}_2$), 137 ($\text{C}_5\text{F}_4\text{H}$), 119 ($\text{C}_5\text{F}_3\text{H}_2$ base), 99 ($\text{C}_5\text{F}_2\text{H}$), 94 ($\text{C}_3\text{F}_3\text{H}$), 93 (C_3F_3), 88 ($\text{C}_4\text{F}_2\text{H}_2$), 81 (C_5FH_2), 80 (C_5FH), 75 ($\text{C}_3\text{F}_2\text{H}$), 69 (CF_3), 68 (C_4FH), 61 (C_5H), 57 (C_3FH_2), 56 (C_3FH), 51 (CF_2H), 50 (CF_2), 44 (C_2FH), and 31 (CF). The ^{19}F NMR spectrum for this compound agreed with published data [11]. Similar analysis of the -78° fraction showed it to be a mixture of unreacted p- $\text{C}_6\text{F}_4\text{H}_2$, the above

described 1H, 4H cyclohexa -1, 4- diene, and a compound of empirical formula $C_6F_8H_2$. An infrared spectrum of the latter compound showed bands at cm^{-1} (intens.): 3070 (w), 2960 (w), 1710 (ms), 1380 (s), 1355 (w), 1260 (m), 1150 (s), 1065 (m), 1030 (m), 743 (mw), 637 (w), 580 (w), and 582 (w). The bands near 3000 cm^{-1} are assignable to $-C=C-H$ and $\geq C-H$ stretches respectively while the 1710 cm^{-1} peak is typical of a $-CF=CH-$ stretching vibration [12,13]. Strong ion peaks in the mass spectrum were at m/e (assign): 226 ($C_6F_8H_2$), 207 ($C_6F_7H_2$), 186 (C_6F_6), 157 ($C_5F_5H_2$), 144 (C_4F_5H), 137 (C_5F_4H), 119 ($C_5F_3H_2$), 117 (C_5F_3), 113 (C_3F_4H), 94 (C_3F_3H), 93 (C_3F_3), 75 (C_3F_2H), 69 (CF_3), 57 ($C_3F_2H_2$), 51 (CF_2H), and 50 (CF_2). The NMR spectrum of the -78° fraction confirmed the presence of p- $C_6F_4H_2$, 1H, 4H-hexafluorocyclohexa -1, 4-diene, and 1H, 4H-octafluorocyclohexene, position of H or F, ppm or δ (rel. area): 1-H, 4.1 (1); 2-F, 121.5 (1), 3-F, 118.1 (2), 4-H, 4.7 (1), 4-F, 134.4 (1), 5-F, 130.3 (2), 6-F, 110.4 (2). Of the starting material, 22% was recovered unchanged. Of that reacted, 47% was converted to $C_6F_6H_2$ and 42% to $C_6F_8H_2$. The balance was not accounted for.

$C_6H_5NO_2$. To a stirred solution of $C_6H_5NO_2$ (10 mmol) in 5 ml HF at -78° was added dropwise over 30 min., a solution of NF_4BF_4 (2.88 mmol) in 5 ml HF. Reaction of the NF_4BF_4 was shown by an increase in pressure due to NF_3 evolution. When all the NF_4BF_4 had been added the reaction was gradually warmed to 0° and left overnight. During the warming, the reaction solution changed from pale yellow to dark brown. Keeping the reaction ampoule at -45° , the NF_3 , HF, and other volatile materials were pumped away through -78 and -196° traps. After the majority of the HF was removed, the reactor was maintained at 0° . Everything that passed the -78° trap was discarded. The -78° fraction consisted of a few droplets of an almost non-volatile liquid. Mass spectroscopy of the vapor from the drops showed minor amounts of aromatic fluorocarbons which did not contain NO_2 substituents. These were of empirical formula $C_6F_nH_{6-n}$ ($n=1-4$). The principal ion peaks observed were m/e (assign.): 85 ($NO_2F \cdot HF$), 49 (NOF), and 30 (NO). Examination of the liquid remaining in the reactor by NMR spectroscopy showed that five fluorinated compounds were present and all were found to be substituted nitrobenzenes by comparison of the observed chemical shifts with reported values [9]. By measurement of the area of the resonances the amount of each compound was

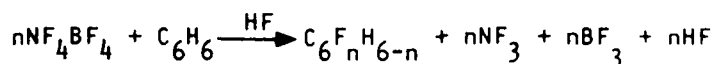
calculated: o-C₆F₄NO₂ (15%), m-C₆F₄NO₂ (62%), p-C₆F₄NO₂ (6%), 2, 6- or 3, 5-difluoronitrobenzene (15%), and 2, 4-difluoronitrobenzene. The large excess of C₆H₅NO₂ employed, and still present, masked the ¹H spectra of these products and thus the ¹⁹F spectra were relied on for identification.

C₆H₅CH₃. Toluene and NF₄BF₄ (1:4 molar ratio) were reacted by condensing the hydrocarbon onto the stirred HF solution of the salt at -78°. Alternatively, toluene in HF at -78° was treated dropwise with a solution of NF₄BF₄ (1:2 molar ratio). In either case instantaneous reaction occurred and the solution became black. After warming to 0° for a few hours, these reactions were worked up in the usual manner. Much tar like residue remained in the reactor in each case. Examination of the volatile species trapped at -78° by infrared spectroscopy showed strong bands near 1500 cm⁻¹ confirming the presence of aromatic species. Mass spectra of these fractions showed in both experiments that only aromatic substitution products were present; these were of empirical formula; C₇F_nH_{8-n} (n= 1-4). The low intensity of the m/e 69 and 51 peaks indicated the probable absence of CF₃ or CF₂H groups in these compounds since the intensity noted for those peaks can well be attributed to C₄FH₂ and C₄H₃ ions. From the reaction using a higher ratio of NF₄ there was found a significant but not large amount of C₆F₄H₂, indicating some displacement of CH₃ from the ring. The NMR spectra of these products confirmed that various fluorotoluenes were present [9], approximately in the amounts given (%); o-C₆F₄CH₃ (15), p-C₆F₄CH₃ (15), m-C₆F₄CH₃ (8) 2, 4-difluorotoluene (30), other di- and tri-fluorotoluenes (25), and 2, 4, 5, 6-tetrafluorotoluene (7).

C₆H₆. Benzene and NF₄BF₄ were reacted using the same two techniques described for toluene. It was not possible to prevent charring and blackening of the benzene. Nevertheless, isolation of the volatile products condensable at -78° and examination of their mass spectra showed that substantial substitution of H by F had occurred, C₆F_nH_{6-n} (n= 1-5). No C₆F₆ was observed and only minor amounts of addition products, C₆F₆H₂ and C₆F₇H.

RESULTS AND DISCUSSION

These experiments show a sharp difference in the reactions of NF_4BF_4 with aromatic hydrocarbons, on the one hand, and with highly fluorinated aromatics, on the other hand. In the case of the hydrocarbons it was found that a vigorous fluorination reaction occurred, even at -78° in HF solution. This reaction resulted in the substitution of F for H on the ring with retention of aromaticity. With high ratios of NF_4^+ to ϕ (~ 3), the number of fluorines substituted was up to 5 in benzene as shown in the general equation:

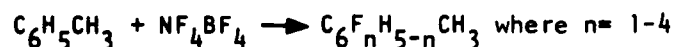


where $n = 1-5$

At the higher ratios of NF_4^+ to substrate the reaction was more difficult to control and more "char" formation was noted. Hexafluorobenzene was not observed even though it is easily detected by mass spectroscopy since its parent ion is the base peak in its spectrum [8]. Only trace quantities of partially saturated species, $\text{C}_6\text{F}_6\text{H}_2$ and $\text{C}_6\text{F}_7\text{H}$, were observed.

In order to determine whether the fluorination was an electrophilic reaction, the reaction of two substituted benzenes, $\text{C}_6\text{H}_5\text{CH}_3$ and $\text{C}_6\text{H}_5\text{NO}_2$ was investigated. These were chosen because of their well known dissimilar activating effects in aromatic substitution processes. Since the CH_3 group is electron donating and the NO_2 group is electron withdrawing, it was anticipated that the ortho-meta-para product distribution would allow distinction between an electrophilic and a free radical reaction path.

The ratio of NF_4^+ to toluene was in the range of 2-4:1, thus, considerable amounts of fluorine were available (assuming one F/NF_4^+ is available for substitution) and multisubstitution was expected. As the result of a very rapid -78° reaction the observed general reaction was:



The low relative intensity of m/e 69 and 51 in the mass spectra of the products, strongly indicated that CF_3 and CF_2H groups were not present. Similarly no other spectroscopic evidence was obtained for CH_3 group fluorination. For mono and di-F products, a typical product ratio was: o-F (15), m-F (8), p-F (15), 2, 4 di-F (30), and mixed di- and tri-F (25). Obviously o- and p-products predominate for this electron rich ring, a result which is compatible with an electrophilic substitution process.

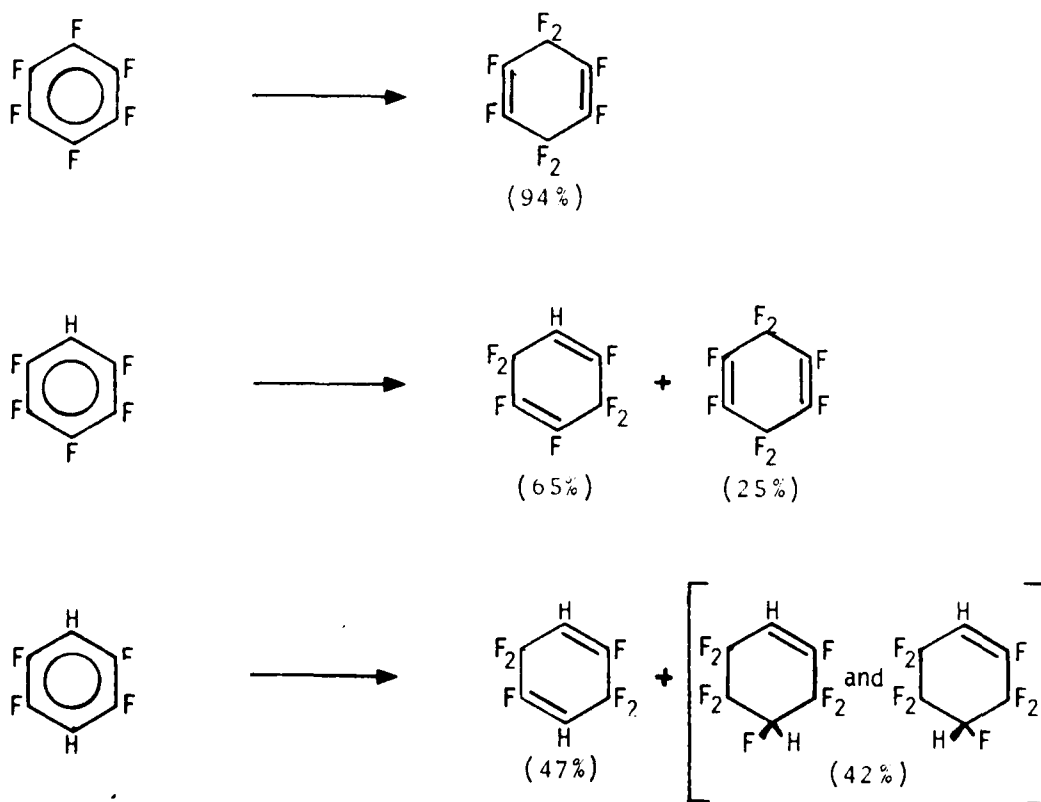
For the nitrobenzene reaction with NF_4BF_4 a (10:3) ratio, respectively, of those reactants was used. Even with a higher concentration of C-H sites of reaction, this reaction was milder as exemplified by a slightly slower NF_3 evolution and the lack of darkening of the solution until the mixture was warmed to about 0° . Fluorine substitution occurred to give $\text{C}_6\text{F}_n\text{H}_{5-n}\text{NO}_2$ ($n = 1-4$) compounds. Minor amounts of $\text{FNO}_2 \cdot (\text{HF})_n$ were formed and traces of $\text{C}_6\text{F}_n\text{H}_{6-n}$ species, but overwhelmingly, the NO_2 was not displaced. The observed products were mainly monosubstituted with the relative amounts being: o-F (16), m-F (62), and p-F (7). The abundance of meta product was consistent with a reaction in which an electrophile attacks a ring substituted with an electron withdrawing group such as NO_2 .

For nitrobenzene a yield of fluorinated products was not determined since only a few volatile products were separated from the large excess of ϕNO_2 . However, in view of the high relative amount of mono-F species and the limited amount of charring, it is believed that the yield was quite high. For the much more reactive C_6H_6 and $\text{C}_6\text{H}_5\text{CH}_3$, yields varied widely. Volatile, fluorinated species were observed equivalent to 30-60% of the starting aromatic compounds.

From these screening experiments it is readily apparent that NF_4^+ salts might be very useful reagents for the preparation of substituted fluoroaromatics, especially when multisubstitution is desired. No evidence for addition reactions was observed until at least 4-5 fluorines had been introduced into the ring. Also, it is apparent that milder, more controlled conditions are required to exploit fully this very active reagent. More dilute solutions and lower temperatures are obvious changes to be investigated. Nevertheless a new method has been discovered for substituting F for H which retains aromatic character and may not adversely effect saturated or oxidized substituents.

To obtain more data on the step-by-step reactions of aromatics with NF_4^+ it was decided to examine systems which were highly fluorinated and thus more inert toward a strongly fluorinating electrophilic reagent. This was also expected to show whether the apparent tendency of these systems to stop at the tetra- or penta- fluoro stage was general.

Experiments were carried out using three different fluoro benzene materials. All reacted gradually at, or near, ambient temperature. The fluorine uptake by the substrates was equivalent to one F/NF_3 and the liberated NF_3 was recovered and measured. All solutions and products were colorless throughout the reactions. Excess, unreacted NF_4BF_4 was recovered and measured to confirm the observed stoichiometry of reaction. The products were identified spectroscopically and many have been reported in the literature, making their identification unequivocal. The overall results are shown by the equations.



For all of the three highly fluorinated benzenes, the addition of the first two fluorines occurs in para position to each other (1, 4 addition) and ortho to any hydrogen, if present. The addition of a second pair of fluorines cannot proceed by a 1, 4 mechanism without changing the ring into a bicyclo form, which is generally encountered only under photolytic conditions. Thus, the second pair of fluorines undergoes a 1, 2 addition to yield a cyclohexene.

For penta fluorobenzene, some substitution was also observed. At this point, we cannot say whether this is the result of a true substitution or of an addition - elimination reaction. In the case of $p\text{-C}_6\text{F}_4\text{H}_2$, the second F_2 addition produces the 1H, 4H-octafluorocyclohexene which has two possible geometric isomers. Trace quantities of the saturated product, $\text{C}_6\text{F}_{10}\text{H}_2$, were also detected by mass spectroscopy.

These addition reactions are novel and offer a controlled high yield path to dienes which have previously only been obtained as parts of complex mixtures [14].

ACKNOWLEDGEMENT

The authors gratefully acknowledge support for this work by the U. S. Air Force Office of Scientific Research under Contract F49620-77-C-0038. We also thank Dr. L. R. Grant for helpful discussion.

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APPENDIX G

REACTIONS OF ELECTROPOSITIVE CHLORINE COMPOUNDS WITH FLUOROCARBONS

Reactions of Electropositive Chlorine Compounds with Fluorocarbons

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Abstract. The reactions of simple chlorine containing compounds of the general composition XCl are reviewed and discussed. The compounds included for review are ClF , R_2OCl , SF_2OCl , CF_3OOC , SF_3OOC , $ClOSO_2F$, $ClOClO_2$, and $ClONO_2$. It is concluded that most of the known reaction chemistry of electropositive chlorine compounds can be rationalized in terms of either addition of $Cl-X$ across multiple bonds or oxidative addition to atoms, such as iodine or sulfur in their lower oxidation states. The observed variety of final reaction products can be explained by a multitude of secondary reactions which can involve either eliminations, further additions or degradations. The observed reactions are easily moderated and controlled and only seldom is no reaction encountered.

INTRODUCTION

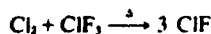
This review is concerned with the reactions of simple chlorine containing compounds of the general composition XCl in which the chlorine atom has electropositive character. The $X^{\delta+}-Cl^{\delta-}$ polarization of the XCl bonds arises from the combination of chlorine with a group of higher electronegativity. The compounds included for review are ClF , R_2OCl , SF_2OCl , CF_3OOC , SF_3OOC , $ClOSO_2F$, $ClOClO_2$, and $ClONO_2$. Except for chlorine monofluoride and chlorine nitrate, these compounds have all been discovered within the last 15 years. Nevertheless during this relatively short period an extensive reaction chemistry has developed involving both inorganic and organic compounds. In particular, the incorporation of positive chlorine species in fluorocarbons and their reactions with fluorocarbons are often unique. This review was written because this area of investigation is most interesting and fruitful and since it has not previously been reviewed.

By virtue of the combination of chlorine with a highly electronegative substituent, all of these materials are medium to strong oxidizing agents. As a consequence of this, care in their handling and use is mandatory. On the other hand, it is this enhanced reactivity which promotes and makes interesting their reactions with the "inert" fluorocarbons.

CHLORINE MONOFLUORIDE

Synthesis and Properties

Chlorine monofluoride was first prepared in 1928 by Ruff and Ascher¹ by a thermal reaction of the elements. Because this reaction can be difficult to control, the alternate method of Schmitz and Schumacher² is commonly used to obtain ClF .



Recent detailed descriptions of this method are available for either flow³ or static⁴ conditions as well as flow conditions for the reaction of the elements.⁵ The low mp ($-156^\circ C$) and bp ($-100^\circ C$) of ClF facilitate its manipulation in vacuum systems and permit contact and mixing under moderating effect of low temperature. Extensive reviews⁶⁻⁸ have been published on the physical properties

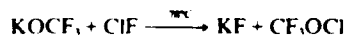
and general chemistry of ClF and other interhalogen fluorides.

Musgrave⁹ has described early reactions of halogen fluorides with organic materials. Others¹⁰⁻¹² have touched on the subject but have been more concerned with systems leading to the addition of the elements of XF ($X = Cl, Br, I$) to organic substrates. The reagents used in the latter reactions are generally not the interhalogen fluorides themselves but rather mixtures of X and F sources such as N -halosuccinimide and HF . The reactions of ClF surveyed in these monographs attest to its oxidizing character and vigorous nature.

Based on the observed reaction chemistry and the common acceptance of fluorine as the most electronegative element, it was a consensus that the direction of the polarization in chlorine monofluoride is $Cl^{\delta+}-F^{\delta-}$. Recently, however, this concept was disputed by Ewing et al.¹⁴ who, based on Zeeman effect measurements, concluded that the sign of the electric dipole in the molecule should be $Cl^{\delta-}-F^{\delta+}$. Shortly after this report, Hartree-Fock calculation by Greene¹⁵ and ESCA results of Carroll and Thomas¹⁶ were published which supported the classical electropositive chlorine concept for ClF . At about the same time, some of the original authors of the Zeeman investigation reexamined¹⁷ their results. While no error in the experimental data was found it was concluded that the marginal nature of the Zeeman dipole measurements was insufficient to prove the direction of the dipole, and that the measurement should be repeated under higher resolution conditions. The ESCA experiments fulfill this need and it is safe to say that the polarity in ClF is as expected. The reactions of ClF with fluorocarbons which reflect this polarity, are divided by type and summarized in the following paragraphs.

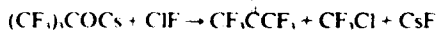
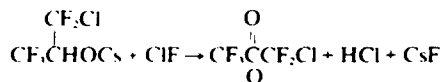
Chlorination

Reactions of ClF which have most often been used to attain chlorination of a substrate are those involving alkali metal salts, $-OH$, and $-CH$ functions. In the case of salts the formation of the alkali metal fluoride provides an effective driving force for the reaction. This method provided the first synthesis of the perfluoroalkyl hypochlorites CF_3OCl ¹⁸ and $(CF_3)_2COCl$.¹⁹

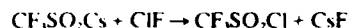


Assurance that only the salt and not its decomposition products, COF_2 and KF , reacted, was achieved by conducting the above reaction at a temperature of -78°C at which no decomposition of the KOCF_3 starting material is possible. The class of R_2OCl compounds, which are themselves positive chlorine species, will be discussed in detail later.

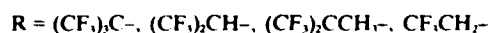
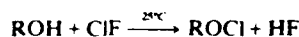
Cesium salts obtained as by-products in fluorocarbon ester reactions were identified by treatment with ClF .²⁰



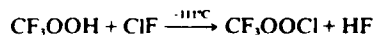
Here one would have expected an alkyl hypochlorite to form. That it was not observed might be due to lack of controlled reaction conditions causing decomposition of the hypochlorites to the products shown. A simple chlorination was noted²⁰ for the trifluoromethyl sulfinate salt.



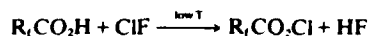
Another effective driving force resulting in chlorination is the formation of HF . Several $-\text{OH}$ compounds have thereby been converted to the corresponding hypochlorites.²⁰



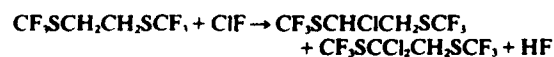
However, perfluoropinacol gave only degradation products while *t*-butyl alcohol reacted explosively. From the successful cases it was concluded that one CF_3 group in the α position is all that is necessary to allow preparation of the hypochlorite from the alcohol. Peroxy hydrogens can also be substituted by chlorine using ClF .²¹



No O-O bond cleavage was observed and thus no CF_3OCl formed. The reported stability of the compound at 25° has not been experienced by others²² although it is sufficiently stable to be synthetically useful as will be shown later. Quite recently DesMarteau²³ has utilized this reaction path to prepare and isolate for the first time, perfluoroacyl hypochlorites.



As expected the compounds have low thermal stability. In addition they are explosive. Displacement of hydrogen from carbon need not occur if a more reactive site is available in the substrate as in the case of the alcohols described above. Lacking the presence of a more reactive group, however, stepwise substitution of H by Cl can occur.²⁴

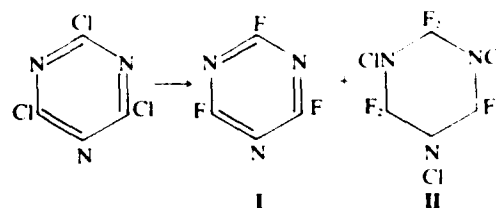


In this relatively uncontrolled experiment, one and two chlorines were substituted onto the same carbon indicating a preferential reactivity. This specificity is further demonstrated by the fact that the sulfur is not affected

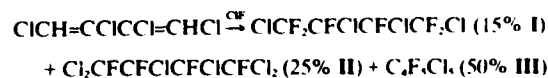
even though sulfur is often attacked and oxidized by ClF in similar compounds.²⁴ Aromatic hydrocarbons have been studied by Gambaretto and Napoli.²⁵ Using stoichiometric quantities, monochloro substitution products were obtained in all cases with yields ranging from 60–80%. Benzene gave chlorobenzene, and toluene produced 2- and 4-chlorotoluene in a 2:1 ratio. Styrene reacted primarily via ClF addition to the olefin side chain, but this was succeeded by limited substitution in the *para* position only. These aromatic chlorinations are indicative of a directed electrophilic attack. In these instances as in others, carefully selected reaction conditions, such as solvents, diluents, and low temperature, resulted in controlled specific chlorine substitution reactions. Furthermore, in all the preceding examples ClF reacted exclusively as a positive chlorine material.

Fluorination

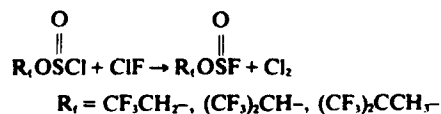
Non-oxidative fluorination. Relatively few cases have been reported in which ClF acts simply as a fluorine substituting agent. One process involving fluorination as a significant pathway is the conversion of cyanuric chloride to the fluoride.²⁶



Pure ClF produced 43% I and 17% II, while pure ClF_3 gave only I but in the same yield. Presumably the nitrogen lone pairs increase the negative character of the ring chlorine thus facilitating its combination with Cl^+ and replacement with fluorine. Perhaps a more plausible explanation for the above reaction is the stepwise addition of ClF across a $\text{C}=\text{N}$ double bond, followed by Cl elimination. Product II could then be obtained from I by a repeated ClF addition. The analogous reactions were observed for the addition of ClF to nitriles. Although not exclusively a fluorination process, the action of ClF on tetrachlorobutadiene has been shown²⁶ to be partially of that nature.



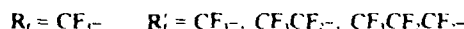
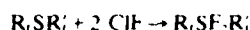
Most probably ClF addition to the double bonds occurred, followed by HF or HCl elimination, followed by further ClF addition. As a net result, fluorination, chlorination, and chlorofluorination all occurred, but the former was dominant. For comparison, ClF_3 gave similar products but the amounts of II and III were reversed as would be anticipated in view of its higher fluorine values. The displacement of chlorine from fluoroalkyl chlorosulfites to furnish the fluorosulfite has been reported.²⁷



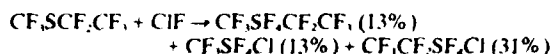
This halogen exchange could not be effected by NaF or KF even at 120°C. Side reactions were not encountered and the fluoroalkyl fluorosulfites were found to have very good thermal stability. All of the foregoing reactions are examples for the replacement of chlorine by fluorine.

Oxidative fluorination. During studies on lower valent sulfur and nitrogen containing fluorocarbons, Shreeve and coworkers have made very skillful use of ClF reactions. Some of their early work has been summarized.²⁸ Basically, it has been shown that ClF is capable of effecting stepwise oxidation of S(II) to S(IV) and S(VI) without large amounts of C-S bond cleavage. Generally, this is achieved through careful reaction temperature control, but sometimes the nature of substituents on sulfur is the dominant factor in determining the final oxidation state of sulfur in the product. Although these are multistep fluorination reactions and probably involve intermediate S-Cl moieties, these have not been observed until the S(VI) stage is attained as in R_2SF_6Cl .

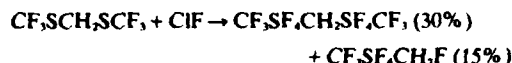
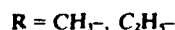
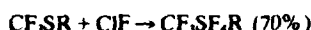
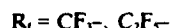
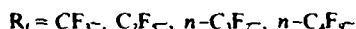
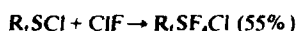
The first report²⁹ of this kind of fluorination used a -78°C reaction temperature which resulted in exclusive conversion of S(II) to S(IV).



Yields were greater than 90% and no C-S bond breakage was noted. In contrast, when conventional fluorinating agents (AgF_2 , CoF_3 , F_2) were employed, only C-S scission and degradation products were obtained. The use of ClF at higher temperatures resulted in additional oxidation^{30,31} furnishing S(VI) derivatives. However, these reactions were now accompanied by significant amounts of C-S bond cleavage.

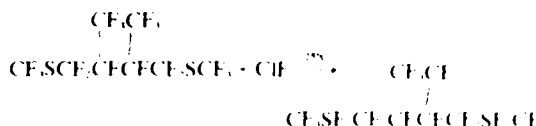


Interestingly, these S(VI) compounds with pseudooctahedral geometry were found by NMR to be mixtures of *cis* and *trans* isomers. These reactions yielded the first examples of the *cis* isomers, since previously published electrochemical methods³² provide only the *trans* isomer. Also, if the substrate for the ClF reaction does not belong to the R_2SR_2 type but has one R_1 replaced by -Cl, -SCF₃,³³ or R^{34} then again only the *trans* isomer is formed.

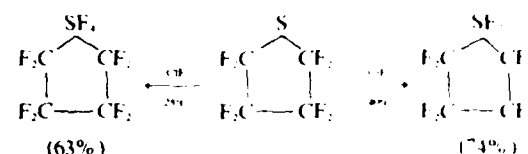


For the R_1SCl and R_1SSR_1 cases there were observed varying amounts of R_1SF_6 products formed by the displacement of Cl by F in R_1SF_4Cl . While in the R_1SR_2 -ClF reaction the intermediate S(IV) products could be isolated, R_1SR_2 and ClF were found to give hexavalent sulfur only, even at low temperature and with less than stoichiometric amounts of ClF. Thus the presence of the

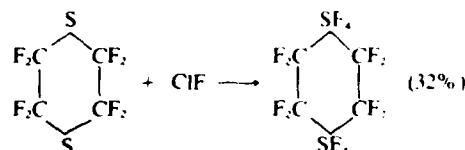
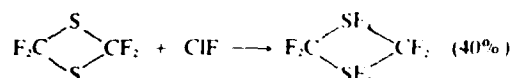
alkyl group promotes considerably the ease of oxidation of the sulfur central atom by this electrophilic reagent. Somewhat at variance with these results are the findings of Haran and Sharp³⁴ that are shown by the equation



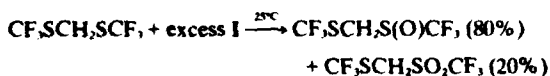
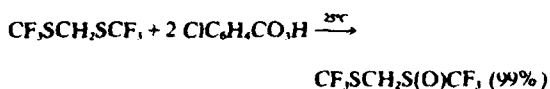
Both sulfur atoms were oxidized but only to S(IV) despite excess quantities of ClF being present. In addition, the reluctance of the sulfur to participate in this reaction is reflected by the fact that 75% of the starting material remained unreacted. Apparently there is an increasing tendency to resist oxidation as the bulkiness of the fluoroalkyl part of the molecule increases. More examples are needed to verify this trend. Cyclic perfluoroalkyl sulfides are also capable of stepwise oxidative fluorination with chlorine monofluoride.³⁵



Again only temperature control is required to produce either an S(IV) fluoride or an S(VI) fluoride in good yield. Similar results were obtained for the room temperature reaction of perfluoro-1,3-dithietane and perfluoro-1,4-dithietane.³⁶

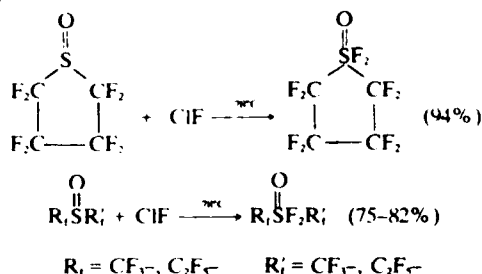


Unfortunately no low temperature experiments were carried out with the dithietanes, but it is to be expected that at lower temperature the sulfur (IV) fluoride analogs of these compounds could be prepared. Once more, it should be noted that in all the fluorination reactions examined involving cyclic or acyclic disulfides, the only products isolated were those in which both sulfur atoms are in the same oxidation state, S(IV) or S(VI). This is characteristic for ClF since other oxidizing agents are capable of forming molecules containing sulfur in two different oxidation states. In particular, *m*-chloroperbenzoic acid has exhibited selectivity in its oxidizing action.³⁷



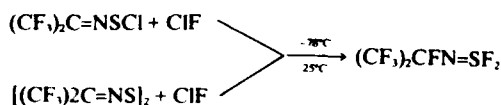
Of the available sulfur atoms only one reacts giving a sulfoxide or a sulfone. This reagent does not oxidize

bis-perfluoroalkyl sulfides. Sulfoxides are susceptible to oxidative fluorination and several examples have been reported.^{35, 36}



Obviously, the fluorination of the sulfoxides is a very facile process as reflected by the low temperature conditions employed and the high yields realized. In fact, higher temperatures lead to C-S bond breaking. It appears that doubly bonded oxygen on sulfur compared to two fluorines enhances appreciably the oxidation from S(IV) to S(VI) by providing increased electron density at the sulfur. This parallels the results for electron donating alkyl substituents on sulfur.³⁴

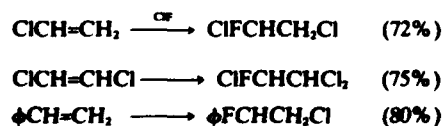
The identification and characterization of the various sulfur (II), (IV), and (VI) fluorides and oxyfluorides is generally quite precise. This is due to the ¹⁹F-NMR chemical shifts characteristic for the various species containing sulfur in different oxidation states. The application of this important tool to these systems has been summarized by Shreeve.²⁸ A final instance of oxidative fluorination of fluorocarbons via ClF has been described for chloro(hexafluoroisopropylideneimino)sulfur(II) and bis(hexafluoroisopropylideneimino)disulfide.³⁷



In each case sulfur (II) is oxidized to sulfur (IV) fluoride by what is effectively a 1,3 addition of fluorine accompanied by a double bond shift and the cleavage of either an S-Cl or S-S linkage. Many other fluorinating agents (e.g. NF₃O, AgF₂, CsF, but not KF) also gave the same fluorination product from the corresponding sulfenyl chloride. Once more, electron donating groups bonded to sulfur are seen to promote oxidative fluorination.

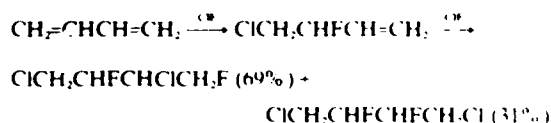
Chlorfluorination

Addition. Saturation of multiple bonds by the addition of ClF represents the most common usage of ClF. Usable multiple bond systems include: C=C, C=O, C=S, S=N, C=N, and C≡N. Some of these reactions require catalysis but most do not. Normally a directed polar addition occurs in high yield but exceptions to this rule are also known. In this section we will be concerned only with simple additions. Systems that also undergo fluorination or extensive bond cleavage will be discussed separately. The use of solvents and cooling permits good conversion of ethylene derivatives to the corresponding ClF adducts without attack on hydrogen.³



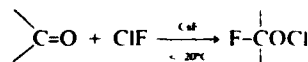
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Markovnikov addition was observed in each case. With butadiene a variety of chlorine fluoride additions ensued³ attributed to a 1,2-Markovnikov addition as a first step followed by an only partially directed second addition



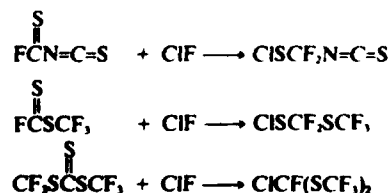
The intermediate is an allylic type olefin and reactions of other allyl substrates were shown also to give mixed Markovnikov and anti-Markovnikov ClF addition products. Calculated electronegativity values for R in the RCH=CH₂ compounds were used by Gambaretto and Napoli to explain the various observed proportions of the different adducts. Boguslovskaya, et al.³⁸ also carried out a study of ClF additions to R-allyl type compounds, correlating the nature of R- with the direction of addition. In all cases mixed adducts were found but in varying amounts. Moldavskii et al.³⁹ as part of a study on perfluoropropene reactivity, showed that ClF forms exclusively *i*-C₃F₆Cl, the Markovnikov predicted product, in greater than 90% yield. Thus with the exception of allylic precursors, the reported ClF additions are overwhelmingly directed electrophilic additions.

Carbonyl groups are not affected by ClF alone. However, in the presence of Lewis bases, such as CsF, they are attacked readily to generate fluorocarbon hypochlorites.



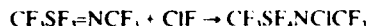
This mode of addition was discovered at nearly the same time by three groups.^{18, 40-42} The French workers' efforts⁴² were limited to CF₃OCl which was first found by them as a secondary product in the reaction of COF₂ and ClF₃ on alumina. Compounds prepared by the base catalysis^{18, 40, 41} were: CF₃OCl, C₂F₅OCl, *i*-C₄F₉OCl, ClCF₂CF(CF₃)OCl, and ClO(CF₂)₂OCl. The intermediacy of R₂O⁺ species is established in these systems and is wholly analogous to the preceding discovery⁴³ of base catalyzed fluorination of carbonyls to give R₂OF products. The induced polarity of the C=O bond together with the fixed dipole of ClF allows only a directed addition to give FC-OCl. In fact, the same net addition was also reported by Fox and coworkers⁴⁴ when strong Lewis acids, such as HF, BF₃, or AsF₅, were present. It was postulated that acid catalysis promoted hypochlorite formation through interaction of the acid with ClF thereby increasing the ClF polarity and reactivity toward carbonyl groups. However, polarization of the carbonyl bond according to ⁺C=O⁻ → AsF₅ cannot be ruled out as an alternative explanation. The interesting chemistry of these hypochlorites will be discussed later.

Thiocarbonyl groups would appear to be ideal candidates for additions of ClF. However, only one report of such interaction has appeared,⁴⁵ the reported reactions being:



Schack and Christe / Electropositive Chlorine Compounds

Catalysts were not required to convert the thiocarbonyl to a sulphenyl chloride. Also, sulfide links and other unsaturation in the starting materials were unaffected by the ClF. Polar additions of ClF to S(VI)=N bonds have been studied by Yu and Shreeve.⁴⁶

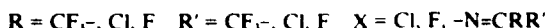
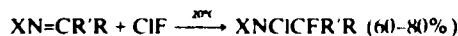
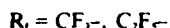


Cesium fluoride may be used to promote this addition, but is not essential. When the double bond involves tetravalent sulfur and nitrogen, ClF causes cleavage (see below). Numerous compounds containing C=N linkages have been investigated with respect to ClF additions. Without exception, these additions are polar and result in saturation of the C=N bond without its rupture. For example, fluorinated isocyanates react as shown:⁴⁷

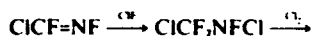


These products are generated at room temperature or below and have typical chloramine reactivity, i.e. with HCl, chlorine is eliminated and the amine formed. Other positive chlorine species, such as Cl₂O and CF₃OCl, are unreactive toward the isocyanates.

Fluorocarbon imines have been extensively studied by Shreeve and coworkers. Acylimines,⁴⁸ haloimines,⁴⁹ and alkylimines^{50,51} all add ClF without C-N bond cleavage



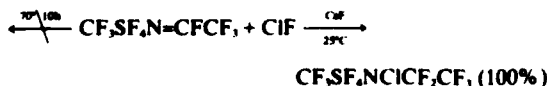
The directed polar additions found do not usually require the presence of a catalyst, such as CsF, to take place unless the imino carbon is peralkylated. Then a catalyst may be necessary. If the product chloramine also has a chlorine bound to the adjacent carbon it can be dechlorinated readily to give a new imine.



Typical alkylimine systems are shown in the equation.



An example⁵² of an imine which even under stringent conditions does not react without a catalyst with ClF is illustrated.

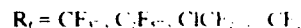
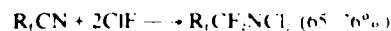


It is also noteworthy that the SF₆-N bond is retained under these conditions while certain SF₆-C or SF₆-Cl substrates⁵³ are subject to significant fluorinative cleav-

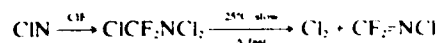
age under milder conditions. Previously, the simultaneous fluorination and chlorofluorination of cyanuric chloride with ClF⁵⁴ had been described. More recently, it has been demonstrated⁵⁵ that cyanuric chloride is an excellent precursor to the same chlorofluorination product



Quite unexpectedly this triazacyclohexane was found to serve as a mild fluorinating agent in several cases, being reduced to (FCN)₃ and Cl₂. It is very rare that C-F bonds function as active fluorine sources. In addition to the many C=N additions cited above it is also well established that nitriles can add ClF.⁵⁶

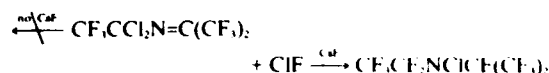


These additions were carried out in the temperature range of 0 to -78°C and no mono ClF adduct could be detected, even when less than a stoichiometric amount of ClF was used. This is caused by the fact that this intermediate imine, -CF₂NCl₂, is more reactive toward ClF than the nitrile itself. Cyanogen chloride behaves similarly, but the chloramine spontaneously dechlorinates.⁵⁷

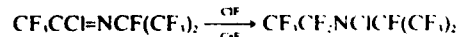
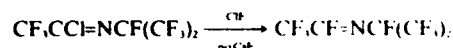


In contrast to this is the thermolysis⁵⁸ of the R₁NCl₂ compounds which require a higher temperature, 200°C, and results in formation of the azo compounds R₁N=NR₁.

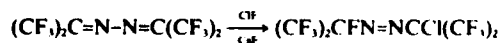
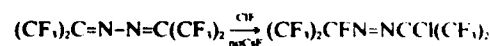
Addition and fluorination. In the addition reactions of ClF occasionally fluorination was also observed and could not be precluded. These limited cases generally involve imino-type unsaturation.⁵⁹



This product is the result of a series of ClF additions and Cl₂ eliminations promoted by CsF. One of the corresponding intermediates has been isolated for the related imine.



Thus the ability to lose Cl₂ from >CCl-NCl- groups plays a dominant role in these cases. Less easily explained is the following azine-ClF reaction.⁶⁰

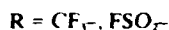
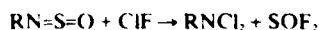


Without CsF, a 1,4-chlorine fluoride addition occurs whereas with CsF a displacement of Cl by F is also encountered. The yield of the latter reaction varied but could not be completely suppressed. Furthermore, CsF and ClF could not be made to give the fluorinated products using the 1,4-ClF adduct as a starting material.

Cleavage of bonds. While the preceding ClF addition schemes involved little or no bond breaking, there are numerous systems in which bond cleavage is the main result of the action of ClF. For example, treatment of KSCN at -30°C gives a variety of products, but none of these retains an S-C bond.⁴¹



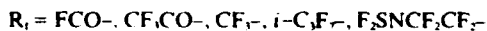
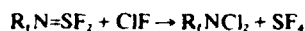
In like manner, sulfinyl amines do not generate any N-S derivatives.⁴²



When ClNSO is subjected to ClF, nitrogen trichloride is a likely intermediate, although it was not isolated.⁴³

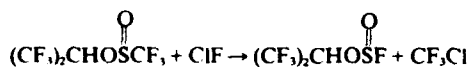


It was always observed that S(IV)-N bonds did not survive the action of ClF. This also appears to hold true for iminosulfur difluorides.⁴⁴

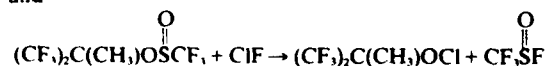


Efforts failed to isolate a mono adduct retaining the N-S linkage.

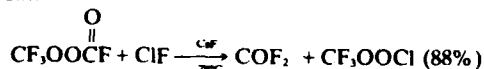
In the discussion of sulfide-ClF reactions, the important bond cleavage reactions of R_2SSR_1 and R_1SR_2 have been mentioned. Sulfinyl esters show at least two different bond breaking paths:²⁰



and



Because this particular process was not studied in much detail, it is not possible to define the conditions favoring either an S-O bond breakage to furnish an hypochlorite or an S-C bond fission to produce a sulfinyl fluoride. A synthetically useful C-O cleavage reaction brought about by ClF was reported for fluorocarbonyl trifluoromethyl peroxide.²²



This procedure simplifies the synthesis of CF_3OOCF_3 by elimination of the previously required intermediate step of hydrolyzing CF_3OOCFO to CF_3OOH .

Summary. It is evident from the above discussion that ClF has recently been successfully exploited in a variety of fluorocarbon reactions. The high reactivity of ClF under a wide range of conditions generally results in good to excellent yields of specific products. Quite often these are unattainable by other means. It is likely that similar judicious applications of ClF to other yet unexplored cases will provide interesting and useful results.

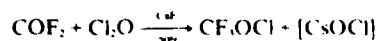
$\text{R}_2\text{OCl/SF}_6\text{OCl}$

The close relationship between the fluorocarbon hypochlorites and pentafluorosulfur hypochlorite permits a joint discussion of their chemistry.

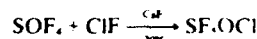
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Syntheses and Properties

The earliest reported syntheses of R_2OCl were base catalyzed ClF additions to carbonyl functions.^{18,45} Although not widely tested, Cl_2O was also used as a positive chlorine source to prepare the trifluoromethyl derivative.⁴⁶



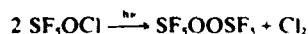
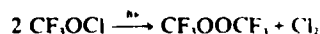
The base catalyzed chlorofluorination process was also applied to thionyl tetrafluoride.^{41,46}



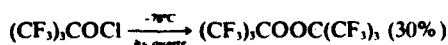
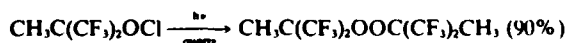
This is directly related to Ruff and Lustig's fluorination procedure⁴⁰ for the synthesis of SF_6OF . Soon after the original reports, acid catalysis was shown to be effective in this hypochlorite formation.⁴⁴ Subsequently, the reaction of ClF and certain alcohols opened yet another route to fluorocarbon hypochlorites.¹⁹ All of these R_2OCl syntheses have been described in the preceding ClF reactions sections. Fluorocarbon hypochlorites and SF_6OCl are colorless liquids and gases. Volatility is related to molecular weight and is consistent with typical covalent fluorocarbons. For example, CF_3OCl has a bp of -46°C and SF_6OCl has a bp of 9°C . The thermal stability of the simpler compounds decreases rapidly from that of CF_3OCl in the following order: $\text{CF}_3\text{OCl} > \text{C}_2\text{F}_5\text{OCl} > i\text{-C}_4\text{F}_9\text{OCl} \sim \text{SF}_6\text{OCl}$. When an α fluorine is not present as in the ROH derived hypochlorites,¹⁹ $(\text{CF}_3)_2\text{COCl}$, $\text{CH}_3\text{C}(\text{CF}_3)_2\text{OCl}$, $(\text{CF}_3)_2\text{CHOCl}$, etc., then they are reported to be stable to at least 80°C . The hypochlorites are all susceptible to hydrolysis which is one of the major problems in utilizing them.

Reactions

General. The R_2OCl and SF_6OCl chemistry encompasses both radical and polar reactions. As part of the characterization of these compounds, the influence of UV photolysis was examined.

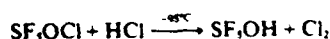
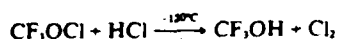


The high yields (90%)^{18,41} of these peroxide forming processes render them useful for preparing these compounds. For CF_3OCl the photolysis has been studied under matrix conditions.⁴² Longer chain R_2OCl with α fluorines give only degradation products attributed to rapid decomposition of the $\text{R}_2\text{CF}_2\text{O}$ radicals. When the alkoxy radicals are stabilized by some special structural feature, then again peroxides can be obtained via photolysis.⁴³



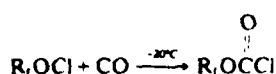
Other radical combinations are also known,^{18,39} e.g. with NF_3 to produce CF_3ONF_2 and SF_6ONF_2 . A reaction directly associated with the positive chlorine nature of the hypochlorites is the increased tendency to combine with negative chlorine. Seppelt has exploited this property as illustrated.^{44,48}

Schack and Christe / Electropositive Chlorine Compounds



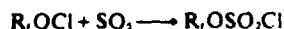
Trifluoromethyl alcohol is the first example of an isolated primary perfluoroalcohol. These have always been considered as nonexistent owing to their ready loss of HF. The thermal stability of CF_3OH is greater than that of SF_6OH (dec at -20° vs. -60°C) even though the former's decomposition is thermodynamically more favored. This has been explained in terms of the longer intramolecular H-F distances in CF_3OH compared to that in SF_6OH .

Oxidation. Spontaneous insertion of carbon monoxide into the OCl bond of these hypochlorites occurs in a near quantitative manner.⁶⁶ This is formally an oxidation of the carbon.



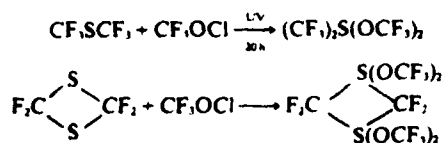
$\text{R}_1 = \text{CF}_3$, C_2F_5 , $i\text{-C}_3\text{F}_7$, SF_6 , $(\text{CF}_3)_3\text{C}$, $(\text{CF}_3)_2\text{CH}$, etc.

Hypochlorites undergo this reaction only with activation, while the best known alkyl hypochlorite, $(\text{CH}_3)_3\text{COCl}$, does not react with CO to 80°C . Fluorocarbon hypochlorites add directly to SO_2 at room temperature or below.^{67,68} Excellent yields of the corresponding chlorosulfate are obtained by inserting the sulfur of the SO_2 molecule into the OCl bond.



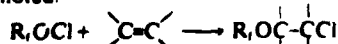
$\text{R}_1 = \text{CF}_3$, $i\text{-C}_3\text{F}_7$, $(\text{CF}_3)_3\text{C}$, $(\text{CF}_3)_2\text{CH}$, $\text{CH}_3\text{C}(\text{CF}_3)_2$, CF_3CH_2

This represents a formal oxidation of S(IV) to S(VI). Under the influence of UV light CF_3OCl has been found to oxidize bis(trifluoromethyl)sulfide and tetrafluoro-1,3-dithietane.⁶⁹



However, the duration of the described experiment seems incompatible with CF_3OCl being the active agent in this oxidation of S(II) to S(IV). Thus, CF_3OCl under UV irradiation decomposes rapidly to CF_3OOCF and Cl_2 . Therefore, unless the oxidation of S(II) to S(IV) occurs quickly it would appear that CF_3OOCF , alone, or assisted by Cl_2 , must be the oxidizing agent.

Addition. The addition of R_1OCl to olefins has been investigated by several groups.^{70,71,72} Rapid reaction was generally noted.



$\text{R}_1 = \text{CF}_3$ Olefin = $\text{CF}_2=\text{CF}_2$, $\text{CH}_2=\text{CH}_2$, $\text{CF}_2=\text{CFCl}$, $\text{CH}_2=\text{CHCl}$, $\text{CF}_2=\text{CH}_2$, $\text{CF}_3\text{CF}=\text{CF}_2$, $\text{CF}_3\text{OCH}=\text{CH}_2$, $\text{CFC}=\text{CFCI}$

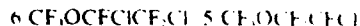
$\text{R}_1 = i\text{-C}_3\text{F}_7$ Olefin = $\text{CF}_2=\text{CF}_2$

$\text{R}_1 = (\text{CF}_3)_3\text{C}$ Olefin = $\text{CF}_2=\text{CF}_2$, $\text{CH}_2=\text{CH}_2$

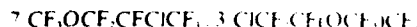
$\text{R}_1 = \text{SF}_6$ Olefin = $\text{CF}_2=\text{CF}_2$, $\text{CH}_2=\text{CH}_2$

Except for CF_3CFCl , $\text{CF}_3\text{CF}=\text{CF}_2$, and $\text{CF}_3\text{OCH}=\text{CH}_2$, one product only was formed in these directed additions.

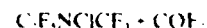
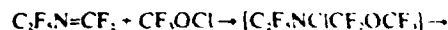
That product was the one predicted on the basis of the chlorine from R_1OCl adding to the most electronegative carbon of the $\text{C}=\text{C}$ bond. Where total direction was not possible the ratio of isomers obtained (if reported) was



and



If the addition was allowed to proceed without moderation, some evidence for dimers and oils was noted,⁷³ thus indicating that R_1OCl is capable of inducing radical chain processes. The high yields (90%) and facile, yet controllable reactions experienced with these systems are contrary to those found for similar CF_3OF^* and SF_6OF^* additions which are extremely difficult to control. As would be expected the fluorocarbon ether products, especially the perhalofluorinated ones have outstanding thermal stability.⁶⁶ Additional 1:1 adducts of olefins and both CF_3OCl and SF_6OCl have been made and a comparison of their properties is being conducted.⁷⁴ Because of their desirable properties, these adducts should be a fertile area for investigation. Of all the olefins examined,⁶⁶ only $\text{CF}_3\text{CF}=\text{CF}_2$ failed to react along with the butyne, $\text{CF}_3\text{C}\equiv\text{CCF}_3$. One additional report on the addition of CF_3OCl to a double bond has appeared.⁷⁵

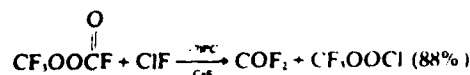
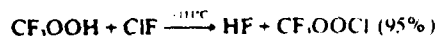


Decomposition of the adduct is surprising. By way of comparison, CF_3OF participates in this reaction only at 250°C and then only to form the fluorinated product, $\text{C}_2\text{F}_5\text{NFCF}_3$.



Syntheses and Properties

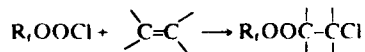
Chloroperoxytrifluoromethane has been prepared by two methods.



The former method²¹ was used for the original synthesis of the compound and gives a purer product. The second route²² presumably proceeds via formation of $\text{CF}_3\text{OOCF}_2\text{OCl}$ which decomposes eliminating COF_2 to furnish CF_3OOCF . Some dispute as to the stability of this pale yellow liquid (bp -20°) has arisen. While Ratcliffe, et al.,²¹ claimed that the compound was stable for prolonged periods at 25°C , Walker and DesMarreau reported only a few hours half life at that temperature.²² Recently, the molecular structures of CF_3OOCF and the related CF_3OOH and CF_3OOF have been determined using gas phase electron diffraction.⁷⁶ For the chloro compound, steric $\text{CF}_3\text{-Cl}$ interactions occur giving rise to two distinct conformers. The synthesis of SF_6OOCF was accomplished⁷⁷ by reactions analogous to those cited above for CF_3OOCF . The starting materials have been reported: SF_6OOH ⁷⁸ and SF_6OOCFO .⁷⁹ Pentafluorosulfur peroxypochlorite was obtained in 70% yield from the hydroperoxide and in 90% yield from the fluoroacylperoxide. It is a straw-yellow liquid with an extrapolated boiling point of 26.4°C but it decomposes rapidly at 22°C .

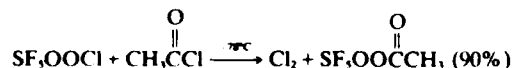
Reactions

The primary reaction mode of these R_2OOCl compounds is the rupture of the terminal hypochlorite bond. Both CF_3OOCl ¹² and SF_6OOCl ¹³ add readily to olefins below 0°C to form peroxides.



$R_1 = CF_3-, SF_6-$ Olefin = $C_2H_4, C_2F_4, C_2F_3Cl, CF_3CH_2, CF_2CHCl, CFHCHCl, cis-CFHCCH$

Yields vary and are usually higher for the CF_3- compound. Normally, where isomers are possible, only one product is formed in agreement with a directed, electrophilic addition. Smaller quantities of R_2O ethers are also obtained. The R_2O ether products are believed¹⁴ to arise from reaction of R_2OCl , a decomposition product of R_2OOCl , with the olefins. The fluorocarbon peroxides that are formed are colorless liquids, stable at 22°C. Perfluoro-2-butyne did not react with CF_3OOCl and neither CF_3OOCl nor SF_6OOCl reacted with perfluoropropene or perfluorocyclopentene. Earlier,²¹ it was shown that, unlike R_2OCl type materials, the R_2OOCl moieties do not insert CO or SO_2 into the O-Cl bond. Peroxyesters can be prepared from SF_6OOCl (and SF_6OOH) via acyl halide reactions²² as shown by the following example:

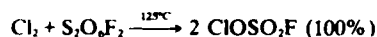


This peroxyester is an ambient temperature stable compound, as are others prepared from SF_6OOH . Clearly, these chloroperoxides behave as positive chlorine species and are useful for the synthesis of many new peroxy derivatives.

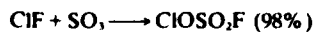
CHLORINE FLUOROSULFATE

Synthesis and Properties

Chlorine fluorosulfate was first prepared²³ by Gilbreath and Cady according to:



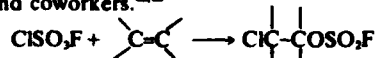
More recently, a more convenient procedure was developed^{24,25} using the readily available SO_3 as a starting material.



Chlorine fluorosulfate is a pale yellow liquid (bp 43°C) which on standing or handling becomes red presumably due to the formation of some ClO_2SO_2F . It is stable at room temperature and has been stored in stainless steel for more than a year without significant decomposition. Nonetheless, it is an extremely reactive material with a host of substrates.

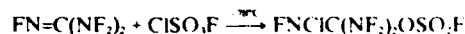
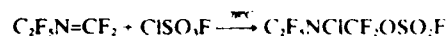
Reactions

Addition. At the time of its discovery, $ClOSO_2F$ (or $ClSO_2F$) was shown to add to olefinic double bonds, i.e. $CF_2=CF_2$.²⁶ Since then, these and similar reactions of $ClSO_2F$ have been studied by Moldavskii²⁷ and mainly by Fokin and coworkers.^{28,29}



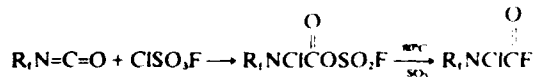
Olefins = $C_2F_4, CFCICFCl, C_2F_3Cl, C_2F_6, (CF_3)_2C=CF_2, C_2Cl_4$

Except for C_2F_3Cl where two isomers were noted, only one product was obtained following Markovnikov's rule. The order of reactivity with $ClSO_2F$ was $C_2F_4 > CFCICFCl > CF_2=CFCl > CF_3CF=CF_2 > (CF_3)_2C=CF_2$. Although this order of reactivity is similar to that observed for nucleophilic reagents, it was speculated³⁰ that the high electrophilicity of $ClSO_2F$ and the formation of isomers with C_2F_3Cl are in keeping with an electrophilic mechanism. Numerous other double bonds are also attacked by $ClSO_2F$. For example imines react at low temperature.^{31,32}



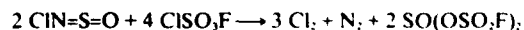
In contrast HSO_3F must be heated to react with $C_2F_5N=CF_2$ and $S_2O_5F_2$ does not react at all.³³ These N-chloro compounds are stable at ambient temperature and are the only products, as expected for a directed polar addition.

Fluorinated isocyanates add $ClSO_2F$ according to:³⁴

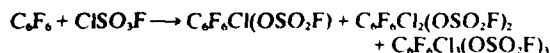


$R_1 = CF_3-, F-$

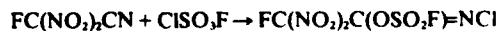
Chlorine monofluoride adducts were similarly prepared³⁵ but other positive chlorine containing molecules, such as $Cl_2O, CF_3OCl, ClNCO$, and $CINSF_6$, did not react. For $CINSO$, the $ClSO_2F$ additions³⁶ were also analogous to those of ClF .



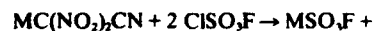
Only 2:1 addition was possible, and the intermediate NCl decomposed to the elements. Most unusual is the ease with which $ClSO_2F$ adds to hexafluorobenzene below 20°C to give 1:1, 2:1, and 3:1 adducts depending on the stoichiometry employed.³⁵



Peroxydisulfuryl difluoride behaves similarly. Both compounds give a *para*-adduct in the 1:1 addition, as demonstrated by hydrolysis to 4-chloropentafluoro-2, 5-cyclohexadiene-one and fluoranil, respectively. These benzene adducts have good thermal stability and are high boiling liquids. Further details on their properties are lacking. The triple bond of nitrile groups also adds $ClSO_2F$ in a 1:1 manner.³⁵

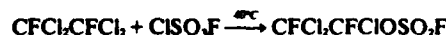


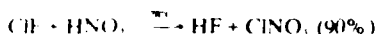
If a cyano salt is involved, both chlorination and addition occur.



It should be remembered that $-C=N$ and ClF reacted only in a 1:2 stoichiometry.³³

Substitution. Fokin and coworkers investigated the replacement of chlorine and iodine by fluorosulfate in selected fluorocarbon halides using $ClSO_2F$.²⁷

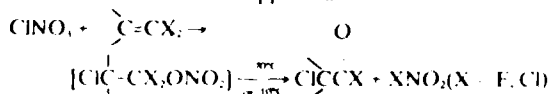




Commercial anhydrous nitric acid may be used. The formed ClNO_2 (ClONO_2) is a pale yellow liquid (bp 23°C) which undergoes slow decomposition at ambient temperatures, but which may be stored indefinitely at -40°C or lower.

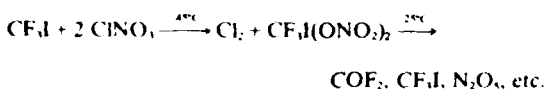
Reactions

Only one report on the addition of ClNO_2 to unsaturated fluorocarbons has appeared³⁰



The vigorous reaction of ClNO_2 with these olefins necessitated dilution with solvents. When two halogens were on the nitrate carbon, the illustrated low temperature decomposition occurred. This instability has discouraged further work on fluorocarbon nitrates.

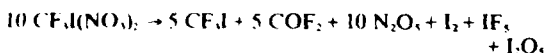
As part of a study on halogen nitrates,³¹ the system $\text{CF}_3\text{I}-\text{ClNO}_2$ was examined with the following results.



Thus, as with Cl_2O_4 , an intermediate oxidized iodo derivative is generated first. Unlike the perchlorate case however, this does not decompose to a stable R_3INO_4 , but degrades as shown. Naumann and coworkers have studied these processes more carefully,³² isolating the $\text{CF}_3\text{I}(\text{ONO}_2)_2$ intermediate and obtaining still another intermediate which they did not isolate.



A thorough, controlled decomposition scheme was worked out for the dinitrato moiety above -20°C involving intermediates, such as CF_3IO and CF_3IO_2 . The overall decomposition equation is:



Raman spectroscopic characterization of $\text{CF}_3\text{I}(\text{NO}_2)_2$, $\text{CF}_3\text{I}(\text{NO}_2)_2$, and related compounds has been reported.³³ Even though ClNO_2 has been available for a number of years, it has not been extensively investigated with respect to fluorocarbons. This might be explained by the apparent instability of the products.

SUMMARY

Most of the known reaction chemistry of electropositive chlorine compounds can be rationalized in terms of either addition of $\text{Cl}-\text{X}$ across multiple bonds or oxidative addition to atoms, such as iodine or sulfur in their lower oxidation states. The observed variety of the final reaction products can be explained by a multitude of secondary reactions which can involve either eliminations, further additions, or degradations. The observed reactions are easily moderated and controlled, and only rarely was no reaction encountered. The $\text{Cl}^{\delta+}-\text{X}^{\delta-}$ polarity of the $\text{Cl}-\text{X}$ bond in these compounds was demonstrated by the "directed" nature of many of the reactions. The strong electrophilic character of these com-

pounds was also evident. Because of the great reactivity of these compounds and the limited amount of work done so far in this area, there are many opportunities for future fruitful research.

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